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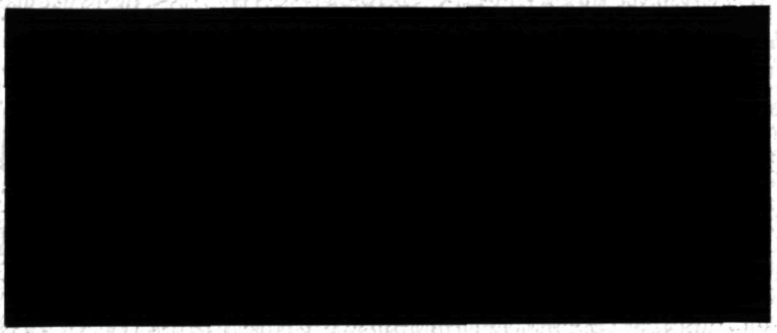

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CONTRACT NAS8-29077

STUDY OF SINGLE CRYSTALS OF METAL SOLID SOLUTIONS

FINAL REPORT

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INTRODUCTION

This document reports and summarizes all work that was performed on NASA Contract NAS8-29077 entitled "Single Crystals of Metal Solid Solutions." The objective of this program was to study the growth of single crystals of relatively high melting point metals such as silver, copper, gold, and their alloys. The purpose was to develop background information necessary to support a space flight experiment and to generate ground based data for comparison. The ground based data, when compared to the data from space grown crystals, are intended to identify any effects which zero-gravity might have on the basic process of single crystal growth of these metals.

The ultimate purposes of the complete investigation are to: determine specific metals and alloys to be investigated; grow single metal crystals in a terrestrial laboratory; determine crystal characteristics, properties, and growth parameters that will be effected by zero-gravity; evaluate terrestrially grown crystals; grow single metal crystals in a space laboratory such as Skylab; evaluate the space grown crystals; compare for zero-gravity effects on crystal characteristics, properties, and parameters; and make a recommendation as to production of these crystals as a routine space manufacturing process.

This particular program encompassed an analytical study of the growth parameters and requirements, and the possible effects of zero-gravity on the growth of the metal single crystals.

Single crystals of pure and doped silver, and 50% (at.) gold-copper alloy were grown by the Bridgman-Stockbarger technique. These crystals were evaluated for defects in the single crystal, material parameters, and crystal growth parameters. A characterization plan for the evaluation of crystals grown in space was written and an ampoule for growing single crystals in space was designed.

REQUIREMENTS FOR CRYSTAL GROWTH IN SPACE OF RELATIVELY HIGH MELTING METALS

Single crystals of metals that are grown in space have at least one growth parameter that is different from earth grown crystals. This parameter is zero-gravity which has a wide range of effects on the crystal growth and the resulting crystal. There are a number of evaluations that must be made in order to determine these effects. These evaluations are required in order to obtain usable information to manufacture routinely single metal crystals in space.

The experimental requirements for growing single crystals of relatively high melting point metals in space can be divided into three main categories. These are: the determination of properties, parameters, and other facts about space grown crystals; the comparison of data from earth grown crystals; and the specifications and design of a space manufacturing facility. Each of these are discussed in the following paragraphs.

The category which needs to be investigated first is that of the crystal properties. All of the crystal properties must be measured for both qualitative and quantitative variances, then a comparison of these properties must be made between terrestrial grown crystals and the space grown crystals. During the comparisons an analysis should be made to determine if there are any crystal properties that are improved by space growth. If there is at least one property that is improved or new in the space grown crystal, it will become advantageous to manufacture such crystals in space. Some of the crystal properties are a function of the growth parameters

and must be determined for growing single crystal metals in space. The initial values and limits will be the parameters as determined by earth based experiments and then modified to meet any requirements not anticipated. All of the final growth parameters in space must be compared to those parameters from the earth based experiments. These comparisons will give relative design information for a space manufacturing facility. Again if there is one parameter that varies widely from the earth based experiments, then a great advantage may exist in the space growth.

A scientific experimental study should be made to determine the exact zero gravity effects on the growth in space of metal crystals. All of the scientific facts, properties, imperfections, characterizations, and parameters of the experiment and crystals should be determined so that a comparison can be made between earth grown crystals and space grown crystals. These scientific studies should be extensive and exact. All facets should be studied in detail so that the subtle differences can be determined.

From all the above information a facility can be designed to accomplish space manufacturing of single metal crystals. This manufacturing facility should incorporate all of the earth based equipment with modifications for growing crystals in space. These modifications should be directed by the growth parameters and space laboratory limitations. From such a manufacturing facility, crystals may be routinely manufactured in space which can be accomplished only if the crystal properties and the growth parameters are known precisely. Other effects which have been studied on previous flights such

as gas bubbles, settling, and surface tension, will try to be supressed or eliminated by experimental design. Thus only the zero gravity effects on crystal growth is utilized.

Space grown crystals may have more uniform properties because of the lack of thermal convection currents. Two such properties might be a more uniform dopant distribution and a more uniform stoichiometry in alloys. This would imply that more of the crystal would be usable because of the less variance along its length. Less variance could also result in unusual or even unknown properties such as electrical, I. R. etc., this is a function of the crystal lattice both microscopically and macroscopically. An example of this is the use of silicon and germanium after the purity had been increased.

CRYSTAL GROWTH METHOD

There are a number of methods which can be utilized to grow single metal crystals. A few of these methods are: Bridgeman-Stockbarger, Czochralski, zone leveling and vapor phase. Growing single crystals in zero-gravity precludes the use of some of these methods such as: Czochralski, zone leveling, any method that requires an open volume above the melt. Since metal single crystals are grown easily by the Bridgeman-Stockbarger method and a sealed capsule can be used in space, this is the method which will be used in this investigation. The Bridgemann-Stockbarger method directionally solidifies the melt by moving the crucible through the furnace from a hot zone to a cool zone. Usually this is done by lowering the crucible in the furnace which solidifies the crystal from the bottom up.

Historically, the method of freezing the melt from the bottom of the crucible has been used for many years by a few researchers. Previous to this the melt was frozen from the top as in normal cooling of an open melt. Bridgemann developed a crucible with a conical bottom, so that the melt would solidify first at the point. This method tended to produce a single crystal. Stockbarger modified this technique by making the cone much deeper and narrower, which starts the crystal growth in a narrow path that blocks some crystal growth orientations. In this way only a small number of seed crystals are formed. As the solidification proceeds, a faster growing seed usually dominates and a single crystal is produced. This method has been modified even further by forming a constriction

in the bottom of the crucible. Thus, in the modified Bridgemann-Stockbarger method there is a seeding chamber at the bottom of the crucible and directly above this is a constriction. This neck allows only one small seed crystal to propagate into the bottom of the main crucible.

In order to cause a melt to solidify from the bottom of the crucible and continue smoothly to the top, the crucible must be cooled from the bottom. This can be accomplished in one of two ways. The crucible may be passed bottom side first through the furnace into a cooler region. Alternatively, the source of heat may be moved from bottom to top of the crucible. Either of these two means results in the melt freezing from the bottom of the crucible.

With either method of solidification the heat source or furnaces must have a temperature gradient. Ideally, this gradient is rather sharp, but not infinitely so. The two temperatures ranges on each side of the gradient must span the melting point of the material. Thus the hot zone is above the melting point and the cool zone is below the melting point, preferably with a centimeter or less between the zones. In order to achieve this gradient, a baffle is usually used between the two zones. A drawing of a typical Bridgemann-Stockbarger furnace is attached to this report.

CRYSTAL GROWTH PARAMETERS

In growing a single crystal of silver or gold-copper alloy there are a number of parameters that must be controlled. The parameters are discussed in the following paragraphs. Before these parameters are delineated it should be noted that there is a restriction on the crystal material; the Bridgemann-Stockbarger method can only be used for materials that shrink upon freezing. Both silver and gold-copper alloy meet this requirement.

The single crystal growth parameters may be separated into categories, those concerning the furnace and those dealing with the material. These will be treated separately.

The furnace parameters are zone temperature, temperature gradient, hold time at melt temperature, pull rate, cooling rate and furnace cut-off temperature. The hotter zone is maintained at a temperature 10 - 80°C above the melting point of the material. If the silver or copper-gold alloy melt is too hot, it supercools as solidification takes place, causing a polycrystalline ingot. The cooler zone is maintained at a temperature 50 - 80°C below the melting point of the material.

The optimum temperature gradient, as well as all other parameters is evaluated by experimental trial and error. A typical value is 30 - 300°C/cm. The temperature gradient and the pull rate are very closely allied. For a gradual gradient a faster pull can be used, and with a steep gradient a slower pull must be used. The pull rate must be such as to cause solidification of the melt

while in the temperature gradient. Ideally, a planar solid-liquid interface is maintained. A typical pull rate is 1 - 10 cm/hour.

The material must be held at the melt temperature for a length of time to insure against cool or hot spots in the melt. Hot spots tend to supercool and cause the ingot to be polycrystalline. If the melt is at too high a temperature it tends to supercool upon crystal growth. With the melt lower than the freezing point solidification occurs through out the melt rather than at the seeding point. This polycrystalline solidification can be triggered by vibration or convection current. Thus the hold time is rather critical so that the melt is the correct temperature and has no hot spots. A typical hold time for the melt is 30 - 60 minutes.

The cooling rate of the lower zone is usually selected so that the crystal is not thermally shocked. This rate normally depends on the thermal insulation of the furnace and the effective insulation properties of the crucible and holder. Thus the cooling rate must be determined experimentally for each furnace-crucible-material system. The cooling rate may be such that the furnace can be turned off instead of cooled at a (50 - 100°C/hr.) programmed rate; in other circumstances, however, such as solid-solid phase transitions, the cooling rate is very important. In such cases as the solid-solid phase transition in the alloy 50% (at) gold-copper, the cooling rate must be determined by experiment.

The material parameters are melting temperature, preferred crystal orientation for growth, occurrence of solid-solid phase

transitions, heat of fusion, tendency to supercooling, sensitivity to vibration during crystal growth, and the distribution coefficient of the dopant or impurity.

The melt temperature and solid-solid phase transitions have been mentioned in the discussion of furnace parameters. Usually a crystal will have a preferred axis for crystal growth purposes, since the atomic and electronic configuration of a certain crystal face may be more conducive to crystal growth. This preferred axis or face will grow at a more rapid velocity than other faces or axes. In the modified Bridgemann-Stockbarger method the crystal orientation surviving the crucible constriction has a high probability of being in the preferred direction.

The rate at which the heat of fusion can be removed from the solid-liquid interface determines the rate of growth of a crystal. This is one reason why the rate of pull must be determined experimentally, since an a priori assessment of the contribution of this effect to the pull rate for various materials would be difficult, at best.

Silver and copper-gold alloy have a tendency to supercool if the temperature of the melt is considerably higher than the melting point at the time of crystal growth. This supercooling is a property of a number of metals and must be considered when melting the material. This tendency is avoided by keeping the hotter zone close to the melting point of the material and allowing the melt to stabilize at the desired temperature.

As the impurity or doping level in silver increases, it is usually harder to grow a single crystal. This is generally caused by the collection of impurities at dislocation faces. Thus, if an impurity is present that is deposited at the freezing interface, it will disrupt the normal silver crystal growth and possibly cause the ingot to be polycrystalline. Slower crystal pulling and vibration free growths may help alleviate this problem. Vibration can cause variations in the crystal such as striation and inhomogeneity because of the atomic kinetics at the freezing interface. The vibration pressure patterns may be radial, or longitudinal which will produce the same type of pattern in the crystal imperfection. The experimental apparatus for growing single crystals should be as vibration free as possible.

TYPICAL EQUIPMENT AND PARAMETERS FOR CRYSTAL GROWTH

In order to grow single crystals of pure silver, doped silver, or gold-copper alloy a specific set of equipment is needed. This equipment is described in general and is presented here only as being typical. The "Multipurpose Electric Furnace System for Space Experiments", proposed for Skylab can be used with a few modifications.

The typical design of the furnace is a resistance type, having two zones with the hotter zone at 1000°C maximum. The two zones should have 60 - 160°C temperature difference with a temperature gradient of 30 - 300°C/cm between the zones. It should have an inside diameter of 4 to 6 cm and a length of at least 25 cm. The inside diameter of the baffle should be approximately 2.5 cm. The ampoule is constructed of graphite sealed in quartz under a vacuum. The maximum diameter of the quartz envelope for the ampoule should be such that approximately 1 mm clearance on the radius exists at the baffle. The length of the graphite ampoule is 8 cm and the length of the quartz envelope just large enough to enclose the graphite and seal.

A smooth operating pull mechanism to pull the ampoule through the furnace, should have a velocity range of 1 to 10 cm/hr. and must be vibrationless. The pull rod must have an attachment for the bottom of the ampoule. A temperature programmed controller must be used to lower the furnace temperature at a steady rate or to hold the temperature at a desired temperature. The increase

or decrease in temperature must be made at a steady rate and have a range capability of 20 - 2000°C/hr. This range is needed first for increasing the temperature at a rate of 1000 - 2000°C/hr. and a second decrease of temperature for annealing of a rate of 20 - 300°C/hr.

The equipment for analysis of the resulting single crystals is briefly noted in the section that relates parameters to materials.

CRYSTAL GROWTH IN ZERO-GRAVITY

The effects of a zero gravity environment upon silver, or copper-gold single crystal growth and crystal imperfection are discussed in the following paragraphs. A few comments are made about the general effects that are caused directly by the lack of gravity. These direct effects which are changes in the crystal growth parameters cause secondary effects in crystal perfection.

In a zero-gravity environment there is, of course, no relative mass acceleration. Density variations in a liquid that give rise to convection currents in a gravitational field have no such effect in the absence of gravity. Convection plays an important role in the production of some of the effects observed in the liquid-solid transition, particularly in the controlled solidification used in crystal growth, so one might expect some differences between crystals grown in a gravitational field and similar crystals grown in the absence of gravity.

A solid usually has a composition different from that of a liquid with which it is in equilibrium, except in the cases of pure materials such as pure silver and solutions exhibiting congruent melting such as 50% (at) Au-Cu. Progressive solidification of a liquid solution, then, usually produces a solid of non-uniform composition, i.e., when solidification is complete, the distribution of a solute in the solid is different from that in the initial liquid, even though the total amount of solute is unchanged. Thus, the effective and equilibrium distribution coefficients are useful in discussing

solidification. The extent to which the component rejected from the solid is mixed with the main body of liquid determines the relation of the effective distribution coefficient to the equilibrium distribution coefficient. This mixing is done by two mechanisms, diffusion of the rejected component into the liquid and the stirring effect of convection currents. In terrestrial grown crystals both of these processes contribute to mixing in the liquid. In a zero-gravity environment, however, diffusion alone would occur.

Theoretically the two cases of mixing by diffusion alone and complete mixing by convection, lead to different predicted values of the effective distribution coefficient. When mixing of the rejected component with the liquid occurs solely by diffusion from a slowly moving planar interface, the value of the effective distribution coefficient is one in the steady state, i.e., the solid formed by a freezing liquid has the same composition as the liquid. Transient effects, caused only by diffusion in a zero-gravity process would produce segregation of impurities and non-uniform concentrations only near the ends of an ingot.

The above discussion applies primarily to alloys such as Cu-Au and to soluble impurities such as dopants in silver. Mixtures in which a component shows limited solubility in either or both phases of a solid-liquid system tend to segregate in the terrestrial environment, with the denser components settling to the bottom of the liquid. In the absence of gravity even mixtures of immiscible components would not

segregate in the liquid phase. Thus macroscopically homogeneous composites and even alloys solidified from homogeneous atomic dispersions of immiscible liquid metals could be prepared in the zero-gravity environment.

The absence of convection currents in a liquid would tend to favor a more stable liquid-solid interface for crystal growth experiments of either silver or copper-gold alloy. If, as is commonly supposed, an unstable interface favors striations and lack of perfection in crystals, crystal growth in zero-gravity should lead to more perfect crystals than those commonly prepared.

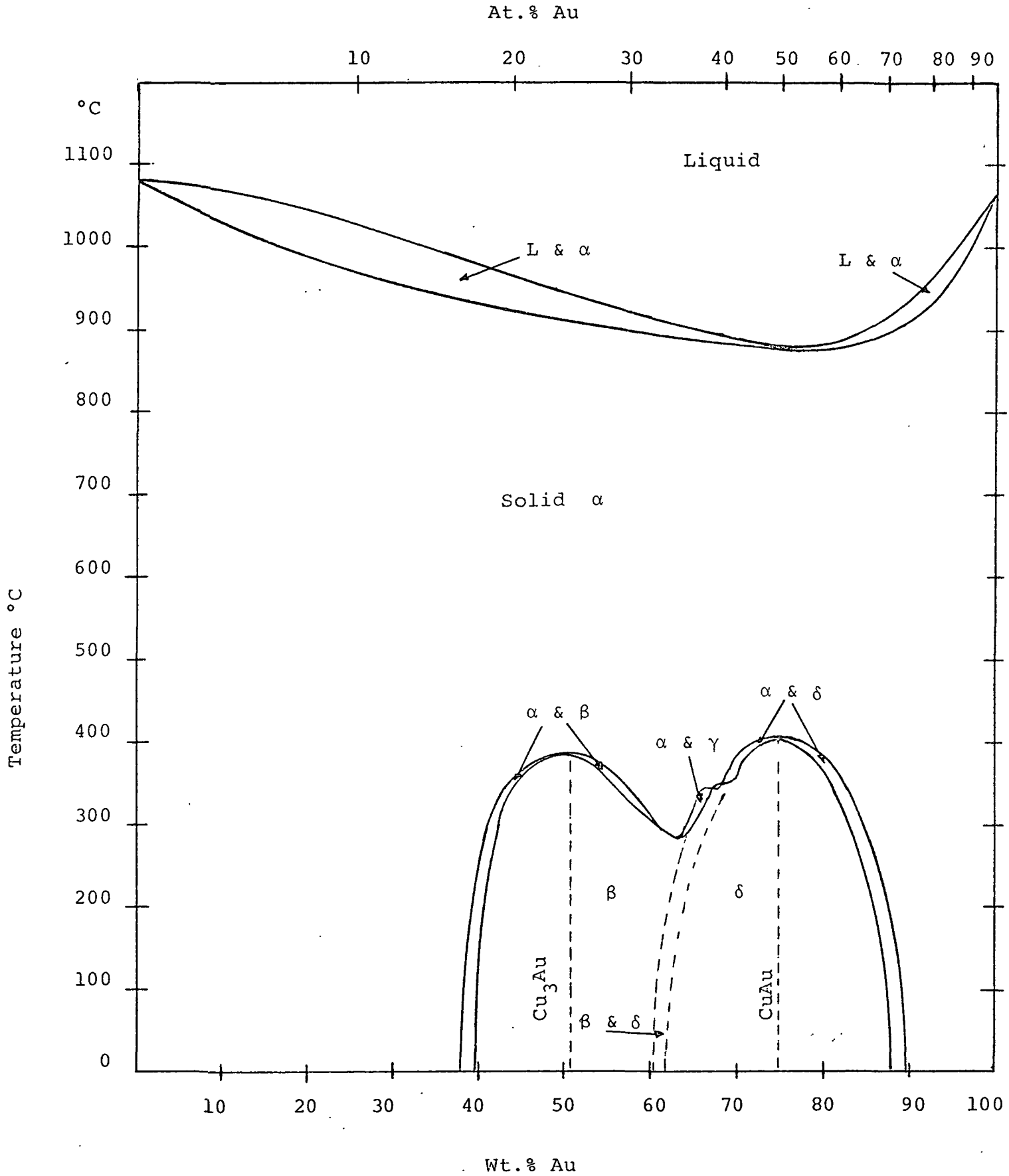
Solidification of alloys that exhibit a eutectic point in their phase diagrams often leads to a lamellar structure. This behavior is a result of properties of the alloy system rather than the particular conditions of solidification. A likely effect of zero-gravity solidification of such alloys is a more perfect lamellar structure rather than a non-lamellar structure. Similarly, if constitutional supercooling is responsible for striations in a crystal, growth in the absence of gravity would not be expected to yield an unstriated crystal. Supercooling of the melt is expected to become more prevalent for a zero-gravity environment.

One obvious disadvantage to crystal growth in zero-gravity arises from the fact that, in the absence of gravity, containerless liquids become spherical in geometry. Even a contained freely floating liquid would contact the crucible wall intermittently, making controlled seeding difficult. A proper container should remedy this

problem. In addition, it would be advantageous if a smooth, vibration-free space laboratory could be achieved. In a vibration-free crucible, the atomic kinetics at the freezing interface are not fluctuating which would yield a more perfect crystal. Vibration in the equipment tends to make crystal imperfections, but in the case of a supercooled melt it also raises the solidification temperature.

SELECTION OF MATERIALS FOR INVESTIGATION

The materials of silver, germanium, and copper-gold alloy were selected for investigation of zero-gravity effects on single crystal growth of relatively high melting metals. This selection was made after a review of all metals and metal alloys that have a melting point between 900°C and 1100°C. A compilation of these metals and alloys has been given previously which gave the alloy, percentage of range for the constituents, and range of the melting curve for the alloy range. A number of candidate alloys were examined and the selection was narrowed to three: Au-Cu, Ag-Au, and Ag-Cu. These three were candidates because of the wider range of constituents. Comparing the phase diagrams for these alloys the Au-Cu has the advantage of a wider constituent range than the other two. It has the advantage of the existence of CuAu and Cu_3Au compounds and the other two do not have existent metal compounds. Each of Au-Cu and Ag-Cu have a point of the melting curve where the solidus and the liquidus lines meet. The advantage of growing a single crystal at this point allows an equilibrium state of equal alloy constituency in the melt and the freezing interface. Thus, no zoning of either constituent and a more uniform stoichiometry. The Au-Cu alloy at a composition of 50% (atomic) is the alloy compound of AuCu and it occurs at the stoichiometry where the solidus and liquidus lines meet. The AuCu compound alloy is an order-disorder alloy due to a lower temperature solid-solid phase transition. This solid-solid phase transition may be affected by a zero-gravity environment during single crystal growth.



PHASE DIAGRAM FOR COPPER GOLD ALLOY

With all of the advantages that the Au-Cu alloy has, it was selected to be the candidate alloy for investigation into the effects of zero-gravity crystal growth in space. The AuCu metal compound was further specified in order to gain all advantages possible from the alloy.

The selection of the elemental metals was greatly simplified since there are only three possible candidate metals: silver, germanium, and praseodyium, see previous paper. There has been more investigation into the properties of single crystal germanium than the other two, so that far more data and growth parameters are known to a better degree of accuracy. These studies have included single crystal imperfections and defects which were related to impurities and growth parameters. The properties of silver are very well known, but those of single crystal silver have not been investigated as thoroughly as germanium. Silver can be easily grown into single crystals for investigation. Silver crystals differ from germanium in that they are soft, whereas germanium is hard, which makes the silver more difficult to cut and polish for an imperfection study. Germanium is a border line metal and is considered a semiconductor.

For the aforementioned reasons both silver and germanium are selected for investigation of zero-gravity effects on metal crystal growth. Silver is suggested for this initial investigation since it is a metal by all definitions.

CRYSTAL PARAMETER MEASUREMENTS AS RELATED TO MATERIALS

There are a number of crystal properties and crystal imperfections that need to be analyzed for the effects of zero gravity. These properties are effective distribution coefficients, impurity segregation, alloy homogeneity, crystal perfection, and the liquid-solid transition. The defects which need to be analyzed are striation, lineage, slippage, lamella, and inhomogeneity. These properties of the crystal will be discussed in the following paragraphs.

In the following discussion there are suggested specific materials for investigation of alloys, pure metals, and doped metals. The specific metals and alloys were selected from the compilation in the previous report because of their characteristics and properties. These materials are to be used for the determination of crystal properties and imperfections which may be affected by crystal growth in zero gravity. These materials were selected from the list given in Appendix A because of a number of reasons which were stated in the previous section.

Alloy inhomogeneity can be macroscopic (about 10^{-1} cm) solute or solvent distributions which are produced in the crystal by various material and growth parameters. On a smaller scale (about 10^{-2} cm) inhomogeneities are produced by fluctuating growth conditions. This causes fluctuating solute concentrations in the crystal which are parallel to the freezing interface. If the freezing solid is supersaturated with one of the alloying elements, the concentration of that

element in the crystal fluctuates with the fluctuating growth parameters. Thus, the inhomogeneities are usually longitudinal with isoconcentrations parallel to the freezing interface but can be random or change radially. To evaluate the homogeneity of a crystal, it must be sectioned vertically, polished, etched and examined visually with a microscope. The material that may be used to measure this property of homogeneity is the (50% at.) gold-copper alloy.

The effective distribution coefficient is a quantitative measure of the ratio of dopant left in the melt to the dopant that is deposited on the freezing interface. This effect is caused by the dopant lowering or raising the melting point of the material. The parameter,used to measure this,is the concentration of dopant along the freezing axis. The concentration distribution can be measured spectrographically and the coefficient calculated. Different spectrographs must be used for different impurity elements and different concentrations. The method to be used would be determined in each individual case. The materials which would yield the greatest amount of information are doped silver or doped germanium.

The impurity segregation in a crystal may be due to either the zoning effect or to convection currents and/or nonuniform thermal parameters. The effect of this leaves the crystal with a distribution of impurities that is nonuniform. This can be

measured in the same manner as the effective distribtion coefficient with a mass, emission, or absorption spectrometer. The materials which are recommended to be used to determine impurity segregation are doped silver or doped germanium.

Crystal perfection is a function of all of the growth parameters and material properties. As the microscopic imperfections build up there are macroscopic imperfections that are produced. The macroscopic properties can be observed by lineage, slippage, lamella, and striations. The microscopic perfection of the crystal can be determined by x-ray backscattering patterns. The materials that can be used for this determination are pure silver, pure germanium, or either doped, or the copper-gold alloy.

The liquid-solid transition is observed by effects on the freezing interface. The morphology of the interface usually depends on: the free energy of the phases; mechanical equilibrium and density gradient of the surface; and the nucleation process of the new surface. The fastest growing crystal axis will dominate the freezing interface. All of the aforementioned points determine the shape of the freezing interface, however none of these can be determined from the interface geometry. The only information that can be obtained from the interface geometry is by comparison with other crystals grown with different parameters. Thus, a comparison between terrestrial grown crystals will yield comparative information about the growth parameters. In order to observe the solid interface the crystal growth must be stopped after the crystal has been partially grown. The only way

that this may be accomplished, in this experiment, is to immediate-cool down the furnace so that the crystal becomes polycrystalline above the previously freezing interface. The crystal is sectioned and polished longitudinally and then examined under a microscope for comparison. The effects of zero gravity on the liquid-solid transition may include slower crystal growth, supercooling, and other effects. Materials which could be used for this study are silver, germanium (either doped or undoped), and the copper gold alloy.

Striations are macroscopic lines along which the composition or the growth rate has a variation. Striations are caused by thermal variances, fluctuations, mechanical variances, bands of impurities that are parallel to the freezing interface, and change in internal stress caused by two vying crystal orientations or compositions. Striations can be evaluated by microscope and etchpit count and geometry. The materials which would be used for striation determination are doped silver or doped germanium, or the copper-gold alloy.

Lineage and slippage are effects caused by internal stress which is due to growth parameter problems. They may be caused by crystal growth patterns (atomic kinetics), or thermal problems. Lineage is caused by thermal fluctuations that are radial across the freezing interface or too fast a cooling rate of the solidified crystal. Slippage is usually caused by vying crystal growth fronts that are secondary to the dominate front, but due to growth conditions are reinforced. Slippage may be caused by the geometry of the freezing interface, fluctuating thermal parameters, or slightly supercooling of the material before solidification. Each of these cause a plane

of discontinuity in the crystal structure and along these lineage or slippage lines, impurities tend to concentrate. Thus, the discontinuity is propogated as impurities add to the internal stress. These lineage and slippage defects can be evaluated by etch pit arrangements. The crystal is cut perpendicular to the growth axis, polished, etched, and examined with a microscope. Lineage is identified by a connected line of evenly distributed etch pits with the same orientation. Lineage lines are usually radial from the central point of the crystal. Slippage lines are identified by a line of randomly distributed etch pits that are randomly oriented. X-ray analysis can be used to supplement the etch pit analysis. The materials that were selected to be used for the lineage and slippage determinations are silver and germanium, either doped or undoped.

Lamella is the layering of the crystal along the direction of the growth axis and can be caused by two phase alloys, thermal convection currents or large slippage planes. With a two phase alloy, one of the phases is continuous and the other has the form of plates in parallel array, or rods in parallel array. These can be caused by unsteady heat flow, freezing interface not flat enough, and characteristic of the material. The effect of this imperfection is a layering of the crystal usually perpendicular to the freezing interface and a periodically variance of the crystal properties. The crystal properties are usually consistent within a layer and the crystal usually has some of its impurities along the lamella surface. The lamella can be determined and evaluated by etchpit analysis and a microscope. The material to be used for the determination is doped silver, or copper-gold alloy.

These are but a few of the crystal imperfections that may be encountered in growing a single metal crystal in a zero gravity environment. These previous paragraphs have tried to describe each of the imperfections and how it is caused, and its effect. A brief statement has been made on how to measure and determine the imperfection, and a metal or alloy, was given as a first trial material. This alloy or metal should be investigated experimentally to determine if all of the above imperfections can be identified. This analysis should be done experimentally to verify this paper study.

SINGLE CRYSTAL GROWTH OF SILVER AND GOLD-COPPER ALLOY

In order to check the results of the analytical study, an experimental investigation was undertaken. Single crystals of silver and gold-copper alloy were grown by the Bridgman-Stockbarger technique and the crystal growth parameters measured. These parameters and requirements were corrected and improved as necessary to fit the particular materials, ampoule, and furnace design used. This part of the study confirmed that single crystals of silver and gold-copper alloy can be grown by this method.

Design, Construction, and Testing of Equipment

In order to grow these single crystals a furnace is needed which would approximate the design of the "Multi-Purpose Electric Furnace System for Space Experiments." However, the detailed information on that furnace was not available so that furnaces were evaluated for this specific experiment. Three different furnaces in which to grow the single crystals were tested considering the space experiment. The first two were constructed without baffles and the third with a center baffle. If a furnace could be used without a baffle then the multipurpose electric furnace for Skylab would be usable without modification.

The first design that was tried had two IR windows of sputtered gold on quartz, through which photographs could be taken of the ampoule and melt as the crystal grew. The furnace had three zones with the windows between the zones. A temperature profile was run and a temperature gradient of 16°C/cm was obtained which was not sharp enough. Figure 1 shows this furnace with

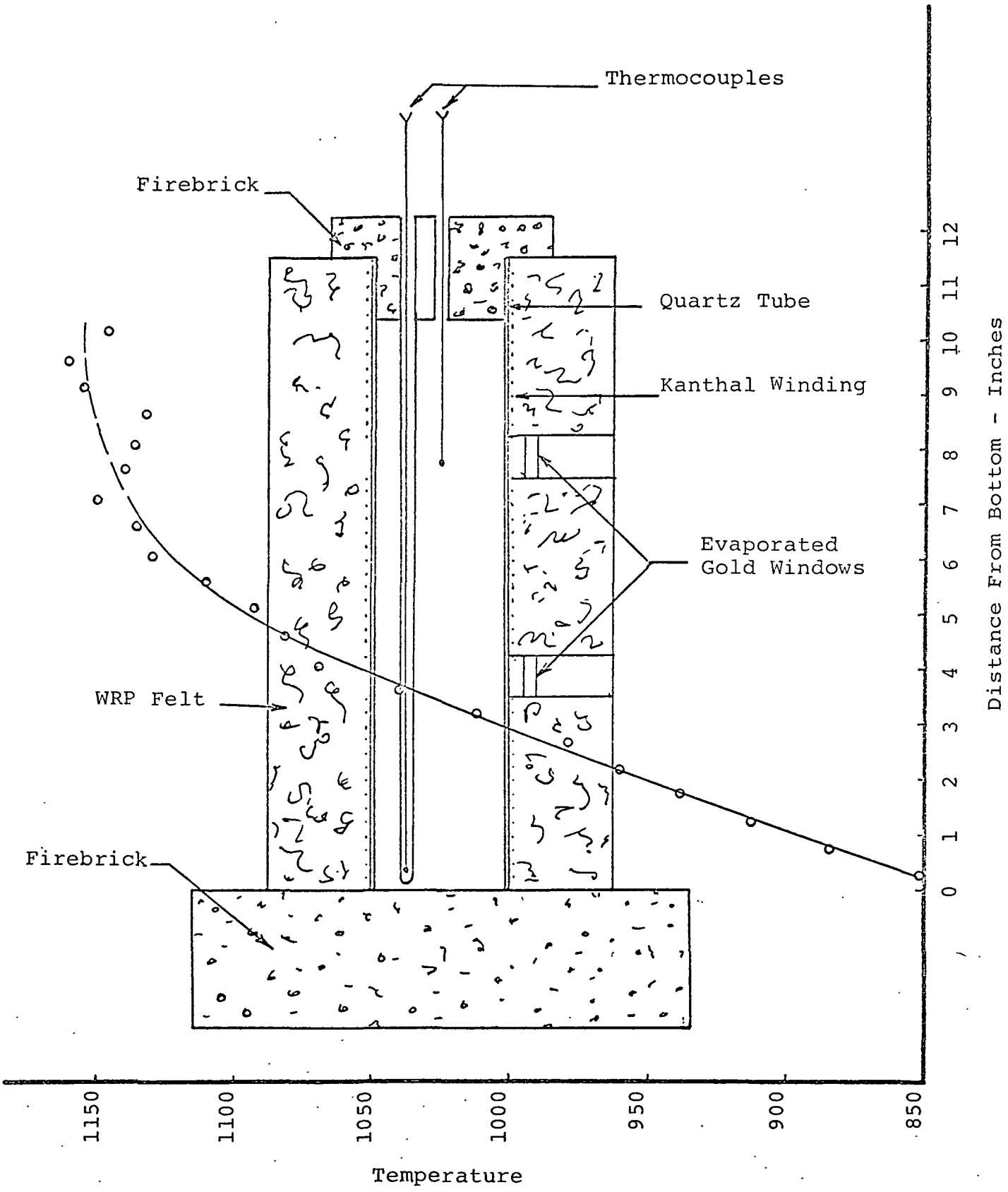


FIGURE 1. SKETCH OF FURNACE #1 AND TEMPERATURE PROFILE

Time	Top Zone					Bottom Zone		Remarks
	Set Point	Current Amps	Temp. Pyro. °C	T.C. MV	T.C.* Temp.	Variac	Current	
1025	000^{1}	4.0	25	1.00	25	63	3	Ref.Jnct. 25°C or 1.00mv,after 1 min set pt 500^{1}, I = 4.4
1030	500^{1}	2.5	280	12.72	312	63	3	Control-set point 990^{1}, I -> 4.4, Variac - > 95, I - > 4.5
1034	990^{1}	4.4	540	21.92	530	95	4.5	Control 1035 - Range 2 - set pt 500^{2} I - > 4.4
1038	500^{2}	4.4	770	31.59	758	95	4.5	Control 1040 - Set pt. 990^{2}
1050	990^{2}	5.0	1000	40.26	973	0	0	Temp. dropped between 1045 & 1050- Action taken as in remark 1-45
1053	990^{2}	4.0	1020	40.74	985	0	0	Controller taking over
1100	990^{2}	4.5	1025	40.74	985	0	0	
1115	990^{2}	4.2	1020	40.82	987	0	0	
1130	990^{2}	4.5	1020	40.85	988	0	0	Start profile
1300	990^{2}	4.5	1020	45.06	1098	0	0	The L&N contact was moved behind wall 110°C error due to ohms Ref. Junct 27°C or 1.08 mv
1350	990^{2}	4.5	1020	45.00	1096	0	0	Power off at 1500 when T. C. broke

Note: *T.C. = Thermocouple

TABLE 1

DATA ON FURNACE WARM UP AND CONTROL

Distance From Bottom	T.C. MV	Temperature °C	Difference from previous temper.	Difference per 0.1"
0.5	35.42	852		
1.0	36.66	882	30	6
1.5	37.84	912	30	6
2.0	38.85	937	25	5
2.5	39.68	958	21	4.2
3.0	40.40	976	18	3.6
3.5	41.58	1007	31	6.2
4.0	42.73	1037	30	6.0
4.5	43.68	1062	25	5.0
5.0	44.32	1078	16	3.2
5.5	44.60	1088	10	2.0
6.0	45.37	1106	18	3.6
6.5	46.04	1124	18	3.6
7.0	46.24	1129	5	1
7.5	46.87	1146	17	3.4
8.0	46.38	1133	-13	-2.6
8.5	46.26	1130	- 3	-0.6
9.0	46.11	1126	- 4	0.8
9.5	46.98	1149	23	4.6
10.0	47.21	1156	7	1.4
10.5	46.23	1129	-27	-5.4

TABLE 2

EXPERIMENTAL FURNACE PROFILE

(First Trial)

Distance From Bottom	T.C. MV	Temperature °C	Difference from previous temper.	Difference per 0.1"
0.5	36.22	872		
1.0	37.30	898	26	5.2
1.5	38.18	920	22	4.4
2.0	38.80	936	16	3.2
2.5	39.48	953	17	3.4
3.0	40.39	976	23	4.6
3.5	41.27	999	23	4.6
4.0	42.20	1023	24	4.8
4.5	43.56	1058	25	5.0
5.0	44.64	1087	29	5.8
5.5	44.92	1094	7	1.4
6.0	45.85	1119	15	3.0
6.5	46.10	1126	7	1.4
7.0	46.36	1132	6	1.2
7.5	45.80	1118	-14	-2.8
8.0	46.13	1126	+8	1.6
8.5	46.62	1140	14	2.8
9.0	46.30	1131	-9	-1.8
9.5		T. C. Broke		

TABLE 2

EXPERIMENTAL FURNACE PROFILE

(Second Trial)

its temperature profile superimposed on the drawing. Tables 1 and 2 show the data taken from one of the runs to determine the temperature profile and other furnace parameters.

The second design was also a three zone furnace except the IR windows were not included. The furnace was connected so that the upper two zones were operating at approximately the same temperature, and the bottom zone adjusted to give a good temperature gradient. Figure 2 illustrates the measured temperature profile of the furnace, showing a temperature gradient of 20°C/cm. This temperature gradient was better than that of the first design, but it was considered to be borderline, since previous analysis determined that 30°C/cm was the minimum. Tables 3 and 4 present the data from a profile determination run on this furnace.

After it was determined that a sufficient temperature gradient was not going to be obtained without a baffle, a design with a baffle was tried. This furnace has two zones that have between them an inconel baffle which completely separates the zones when the ampoule is present. Figure 3 shows a drawing of this furnace and Figure 4 shows its temperature profile. A temperature gradient of 75°C/cm was measured, which is within the desired range. This furnace is capable of temperatures over 1100°C and a tempeature difference between the two zones of 200°C. The heating elements were Electro-Applications, Inc. type X-16 and Y-16, which are semi-circular in shape.

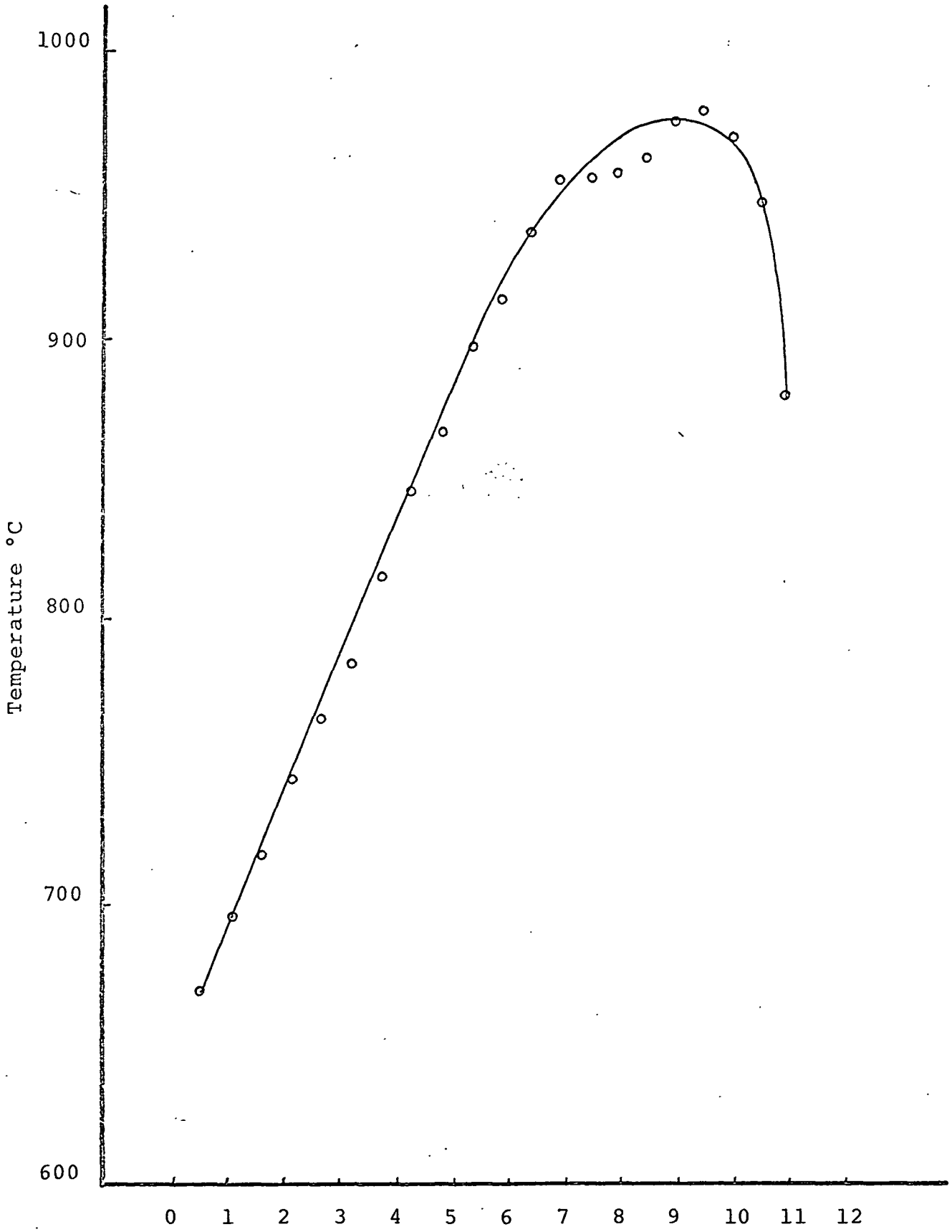


FIGURE 2. TEMPERATURE PROFILE - FURNACE #2

Time	Top Zone					Bottom Zone		Remarks
	Set Point	I Amps	Temp Pyro. °C	T.C. MV	T.C. Temp.	Variac	Current	
1100	000[1]	1	RT	1.04	26	35	2	Power on - Begin slowly adjusting set pt. and current
1105	400[2]	0	200	11.15	274	85	5	Adjust set point-Adjust(min.power) 2.5A
1110	400[2]	5	520	22.96	554	84	4	Continue adjusting
1115	990[2]	4.9	850	35.20	846	95	4.2	Waite - Turn off bottom zone
1120	990[2]	3.9	975	39.34	950	0	0	Control begun.Min current may be high
1125	990[2]	4.0	960	39.12	944	0	0	May have over shot a little - Honeywell - 41.50
1130	990[2]	4.0	980	39.87	963	0	0	Jump in temp but control (green arrow still in middle)
1200	990[2]	4.0	1010	40.88	989	0	0	Honeywell 42 mv-Adjustments being made
1215	990[2]	4.0	1020	40.98	992	0	0	Adjustments have been made - Monitor to see how varies
1230	990[2]	4.0	1020	40.90	990	0	0	Two degree difference
1245	990[2]	3.8	980	39.80	961	0	0	29° drop - adjustment? Green arrow right of red center
1300	990[2]	3.8	975	39.38	951	0	0	Steady decline - joggled red back and forth
1310	990[2]	3.8	975	39.42	952	0	0	Honeywell not showing variation ?
1325	990[2]	4.0	1000	40.56	981	0	0	Not stabilizing - Tried more adjusting
1335	990[2]	4.	1010	40.66	983	0	0	Green arrow staying nearer red

Continued on next page

TABLE 3

FURNACE WARM-UP AND STABILIZATION

Time	Top Zone Set Point	I Amps	Temp Pyro. °C	T.C. MV	T.C. Temp.	Bottom Zone Variac	Current	Remarks
Continuation								
1335	990[2]	4.	1000	40.73	985	0	0	At 40.73 mv green arrow was exactly in center
1400	990[2]	4.	1020	40.72	985	0	0	Temp. profile.
1415	990[2]	4.	1020	40.72	985	0	0	Temp. holding well
1430	990[2]	4.	1000	40.50	979	0	0	Ref. junct.temp 28°C - Ambient changed
1445	990[2]	4.	1000	40.68	984	0	0	Current adjustment had been made - maintains 4 amps
1500	990[2]	4.	1020	40.85	988	0	0	
1515	990[2]	4.	1010	40.82	987	0	0	Profile temp.
1530	990[2]	2.5	1020	40.74	985	0	0	Second profile.
1600	990[2]	3.8	1020	41.02	992	0	0	Power off

TABLE 3

FURNACE WARM-UP AND STABILIZATION

Distance From Bottom	Pyro met. °C	T.C. MV	T.C. °C	Difference from previous temper.	Difference per 0.1"
0.5	675	27.82	669		
1.0	700	28.88	694	25	5
1.5	725	29.83	716	22	4.4
2.0	750	30.92	742	26	5.2
2.5	775	31.76	763	21	4.2
3.0	800	32.60	783	4.	
3.5	830	33.91	815	32	6.4
4.0	870	35.22	847	32	6.4
4.5	840	36.07	868	21	4.2
5.0	920	37.26	898	30	6.0
5.5	930	37.90	914	16	3.2
6.0	955	38.90	938	24	4.8
6.5	975	39.61	956	18	3.6
7.0	975	39.60	956	0	0
8.0	980	39.78	961	3	0.6
8.5	1000	40.30	978	17	3.4
9.0	1000	40.38	980	2	0.4
9.5	1000	40.16	970	-10	-2.0
10.0	975	39.30	948	-22	-4.4
10.5	900	36.58	880	-68	-13.6

TABLE 4

TEMPERATURE PROFILE MEASUREMENT

Continued

Distance From Bottom	Pyromet. °C	T.C. MV	T.C. °C	Difference from previous temper.	Difference per 0.1"
0.5	675	27.70	66.6		
1.0	700	28.76	691	25	5
1.5	725	29.58	710	19	3.8
2.0	750	30.81	740	30	6.0
2.5	775	31.54	757	17	3.4
3.0	810	33.04	794	37	7.4
3.5	850	34.20	822	28	5.6
4.0	875	35.41	852	30	6.
4.5	900	36.30	874	22	4.4
5.0	925	37.59	881	7	1.4
5.5	950	38.50	928	47	9.4
6.0	975	39.24	947	19	3.8
6.5	990	39.78	961	14	2.8
7.0	990	39.92	964	3	0.6
7.5	990	39.88	963	-1	-0.2
8.0	990	39.96	965	+2	0.4
8.5	1000	40.26	973	+8	1.6
9.0	1005	40.52	980	+7	1.4
9.5	1010	40.70	984	+4	0.8
10.0	975	39.44	952	-32	-6.4
10.5	920	37.08	893	-59	-11.8

TABLE 4 (continued)

TEMPERATURE PROFILE MEASUREMENT

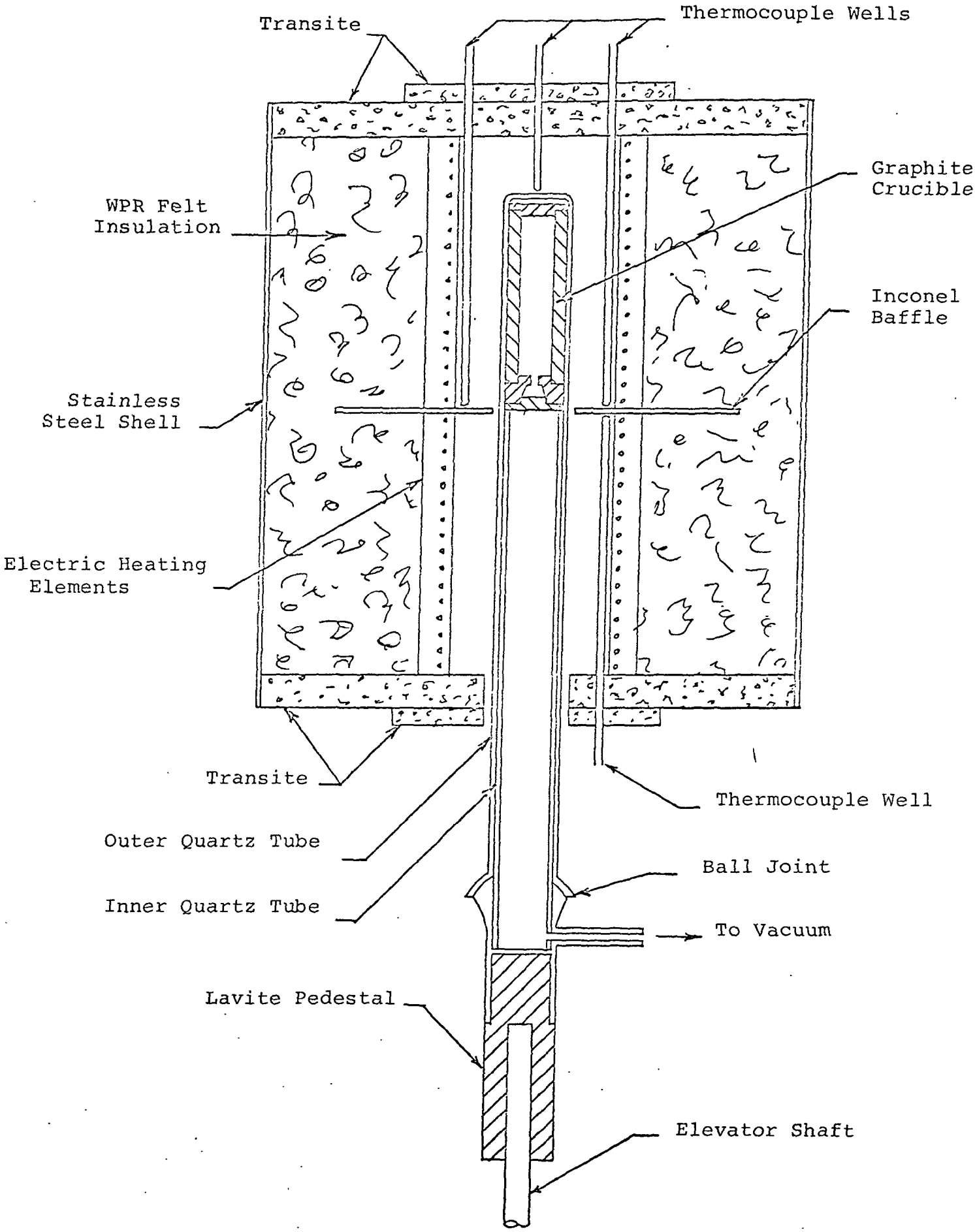


FIGURE 3. BRIDGMAN-STOCKBARGER TYPE FURNACE

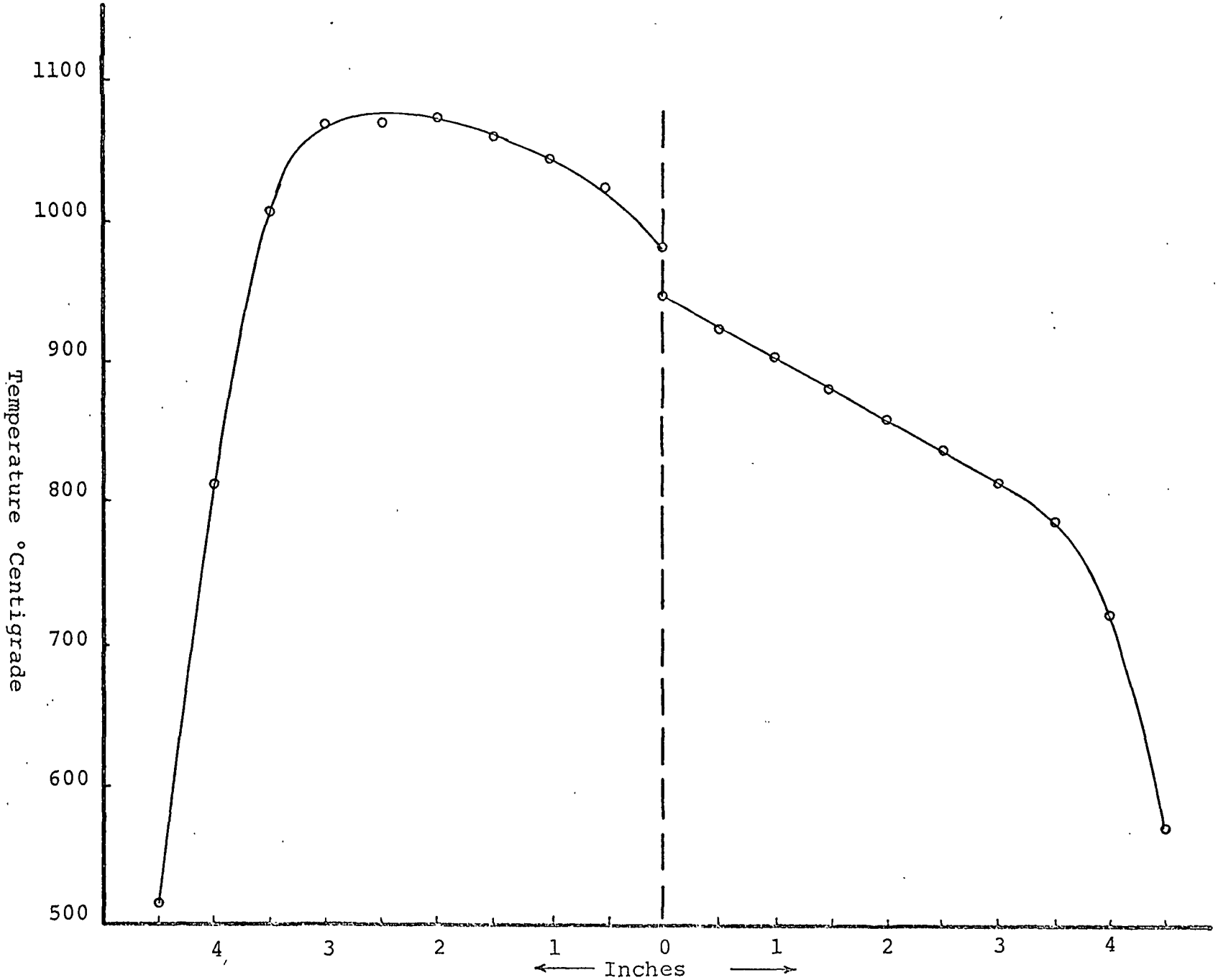


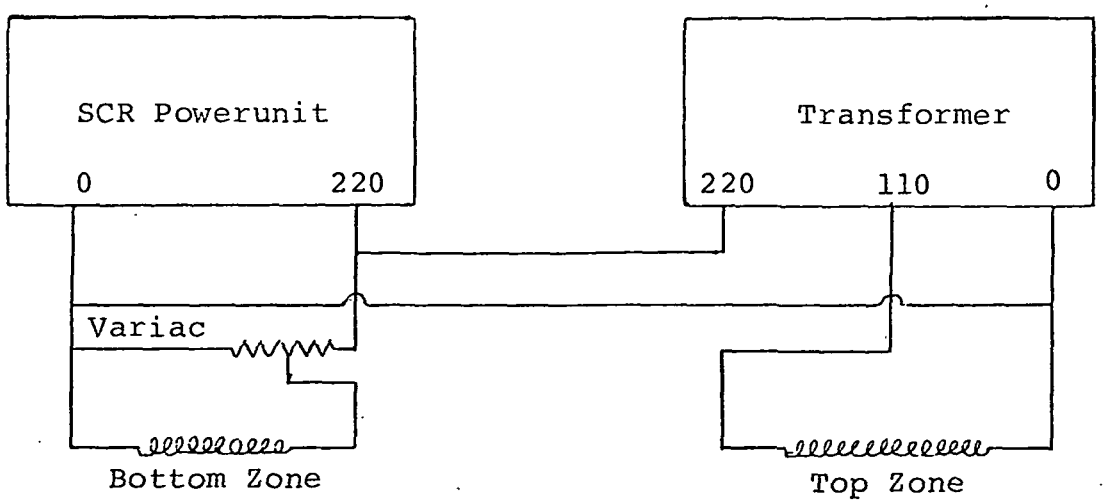
FIGURE 4. TEMPERATURE PROFILE - CRYSTAL GROWTH FURNACE

The heating element specifications are:

Type: X-16	295 watts	@ 1000°C
Type: Y-16	355 watts	@ 1210°C
Voltage rating	57.5 volts	
Length	4.0 inches	
Outer diameter	3.25 inches	
Number of grooves	12	

The two X-16 elements were wired in series for the bottom zone and the two Y-16 elements were wired in series for the top zone. The series connection allowed for operation with 115 volts applied. These elements were wrapped with WRP high temperature fibrous insulation felt, separated by the inconel baffle, and then placed into a steel case. The top and bottom of the steel case were closed with 0.5 inch transite.

The furnace was connected to a West Instrument Company model SCR Powerunit, which supplied 220 volts. A transformer and variac were used as shown in the following wiring block diagram.



During the design checks of the furnace, an ampoule was designed and tested. The silver and the gold-copper alloy wet quartz, but did not wet or stick to graphite, so that graphite was selected for the ampoule material. In order to seal the ampoule a quartz envelope was used. This seal envelope was replaced later by a quartz tube with a vacuum pump attached. This was done in order to save time and quartz when loading and removing the crystal. The ampoule design is described in another section of this report.

A pull mechanism was designed and constructed for lowering the ampoule in the furnace. The mechanism has to be as vibration free as possible in order not to disturb the crystal growth. The drive for the pull mechanism is a B & B Control 1/20 h.p. D. C. motor with a continuous speed range from stall to 173 rpm. It has a drive reduction of 10:1 and operates through an oil filled 25:1 gear reduction box. The lift mechanism is a 3/8 inch screw rod that is rotated by a belt to the gear reduction box.

After the design and construction of the furnace, it was tested in general as described previously. With the baffled furnace the specific characteristics were determined. The capabilities of the furnace and associated equipment, with a loaded ampoule, are:

- Usable temperature range 100°C - 1200°C
- Zone temperature difference 0°C - 200°C
- Temperature gradient at baffle 0°C/cm - 300°C/cm
- Pull mechanism - continuously variable from 0.7 cm/hr to 55 cm/hr

- Cooling rate - manually controlled
- Baffle hole diameter 2.54 cm (1 inch)
- Furnace length 25.4 cm (10 inches)
- Power control - Gulton - West. Model PSCR - 15 - 240 with AA 0344 current limiter

GROWTH OF SINGLE CRYSTALS

Trial runs were made on scrap silver while determining the characteristics of the furnace system and the Bridgman-Stockbarger ampoule. These crystals were polycrystalline, probably because of impurities or from adjusting the different parameters and getting all the"bugs" out of the system and procedure. After the furnace system was debugged, six crystals were grown from scrap silver and each of these polycrystalline. Using pure silver, the growth conditions were optimized and a number of single crystals were produced. Three subsequent runs using these optimum parameters and procedures with scrap silver always produced polycrystalline ingots. This implies that the impurities in the scrap silver inhibit single crystal formation.

In establishing growth parameters fourteen (14) crystals of high purity (99.9995%) silver and twenty three (23) crystals of high purity gold-copper alloy were produced. In these runs 12 silver single crystals and 10 gold-copper single crystal were produced. The range of the growth parameters that were used to grow single crystals of silver are:

- Upper zone temperature 975°C - 1005°C
- Temperature difference of zones 52°C - 73°C
- Temperature gradient 81°C - 115°C/cm
- Hold time at melt temperature 1 hour
- Pull rate 2.3 cm/hr - 6.7 cm/hr
- Pull length 8 cm

- Cooling rate 432°C/hr - 515°C/hr
- Temperature at power cut-off 552°C - 606°C
- Vacuum in ampoule 0.03 Torr - 0.09 Torr

The range of the growth parameters that were used to grow single crystal gold-copper alloy are:

- Upper zone temperature 895°C - 915°C
- Temperature difference of zones 50°C - 78°C
- Temperature gradient 78°C/cm - 122°C/cm
- Hold time at melt temperatures 1 hour
- Pull rate 3.3 cm/hr - 11.7 cm/hr
- Pull length 8 cm
- Cooling rate 160°C/hr - 310°C/hr
- Temperature at power cut-off 295°C - 360°C
- Vacuum in ampoule 0.03 Torr - 0.09 Torr

These were established while checking and improving the growth parameters as determined by the analytical study (Task I) of this program.

The procedures for single crystal growth are the same for both silver and gold-copper alloy:

- Evacuate the ampoule envelope and flush with helium twice and then evacuate the ampoule envelope for use
- Position ampoule in the upper half of the furnace with the lowest part of the ampoule immediately above the baffle

- Place in manual control with equal power to both zones and turn on the West Power unit to approximately 5.4 amperes
- Approximately at 20°C above the melting point set the West Power unit to automatic control and decrease the power to the lower zone to approximately 1.3 amperes
- Start melt time and adjust lower zone temperature to the desired level
- With the zones established and after an hour has elasped, start the pull mechanism to lower the ampoule at the preselected rate
- Turn off the pull mechanism after 8 centimeters of travel
- Decrease the furnace temperature at the predetermined annealing rate
- Turn-off the electrical at the West Power unit below the minimum anneal temperature

The laboratory notes and data from a typical single crystal growth are given in Table 5. These notes were taken from the lab notebook after the procedure had been established but before it became routine.

The possibility of single crystal growth of both pure silver and the 50% (at.) gold-copper alloy was confirmed by the growth of twelve single crystals of the former and ten single crystals of the latter during this phase of the program.

Time	Top Zone					Bottom Zone					
	Pyro meter °C	T.C. MV	T.C. °C	I Amps	V Volts	Pyro meter °C	T.C. MV	T.C. °C	I Amps	V Volts	Set Point
1000	25°C	0.88	21°	3.2	105	25	0.88	21	3.1	105	560
1030	950	38.94	940	3.1	105	925	38.36	925	3.1	105	560
1040	1025	41.68	1010	2.6	74	1000	40.53	980	2.6	85	560
1045	1025	41.46	1004	2.9-3.0	92	975	39.80	961	2.4	75-60	560
1100	1025	41.44	1003	3.0-3.0	96-96	960	39.20	946	1.9-1.5	60-50	560
1110	1015	41.10	994	3.1	105	945	39.04	942	1.6-1.5	50-50	560
1120	1010	41.12	995	3.1	107	945	38.44	927	1.5-1.4	50-40	560
1140	1005	40.74	985	3.1	107	935	38.24	922	1.35	40	560
1200	1005	40.72	985	3.0	102	935	38.06	918	1.35	40	560
1300	1005	40.68	984	3.1	105	930	37.94	914	1.4	40	560
1315	1005	40.91	990	3.0	103	930	38.14	920	1.35	40	500-560
1322	920					865					450-500
1327	850					800					400-450
1335	785	32.22	774			725	29.95	719			350-400
1345	700	28.90	694			655	26.79	644			300-350
1355	625	25.75	620			575	23.56	568			250-300
1405	570	23.26	562			520	20.96	508			250

See Comments on next page:

TABLE 5

DATA ON SINGLE CRYSTAL GROWTH OF SILVER

(TYPICAL)

Time	COMMENTS
1000	Power on - Adjusted zones to equal power. Power unit output 5.4 amps
1030	Green arrow reaching neighborhood of markings around O on set point unit.Switched
1040	to auto.
1045	Set point reached. Begin 1 hr melt time. Adjust power in lower zone downward V->70
1100	Decreased power to bottom zone again. 43°C difference
1110	" " " " " " 58°C difference Power unit 3.3 amps
	" " " " " " 52°C difference " " 3.4 amps
1120	" " " " " " 68°C difference
1140	Began pull - speed control 1.5 - scale read 3 1/4"
1200	Scale on pull 3 15/16" vacuum 0.09 Torr Pull rate about 2 1/6" hr
1300	Scale on pull 5 7/8"
1315	Pull scale - 6 3/8 stop pull begin anneal
1322	Going at a faster rate than program states. When power returns set point lowered
1327	Slow down a bit after this
1335	20 minutes -top zone 216°C prop - bottom zone 201°C - drop or 108°C + 100°C/10 min.
1345	Top zone 80°C drop bottom zone 75°C drop
1355	Top zone 74°C drop bottom zone 76°C drop
1405	Power off - Vacuum shut off at 1500 and introduce He into system

TABLE 5

DATA ON SINGLE CRYSTAL GROWTH OF SILVER

SINGLE CRYSTAL GROWTH OF DOPED SILVER

To gain information about crystal growth parameters, single crystals of doped silver were grown and evaluated. The purpose of this task was to determine the optimum doping level, i.e., the amount of dopant that yields information about these parameters and also produces single crystals consistently.

Two dopants were used in two different sets of growth trials. Single crystals were grown from germanium doped silver and from gallium doped silver. The dopant level was increased from one crystal growth to the next so that a series of crystals were grown, each of which could be evaluated and compared to the previous crystal.

Each of the single crystals (doped silver or gold-copper alloy) was to have been evaluated to obtain the following properties:

- Effective distribution coefficient
- Impurity segregation
- Striations
- Lamella
- Alloy homogeneity
- Crystal perfection

These parameters were to have been identified by the methods described in a previous section of this report.

The method that would have been used to determine an optimum doping level is an iterative process. The general procedure which was established for this determination is presented in outline form below:

- Weigh silver charge and dopant
- Place both in the crucible/ampoule
- Prepare ampoule for crystal growth
- Melt silver and dopant together and hold for one hour (to allow for mixing) and cool rapidly (repeat this step)
- Melt doped charge for single crystal growth
- Grow single crystal
- Evaluate single crystal
  - (i) sample at 3 places (0.1, 0.5, 0.9 of the length)
  - (ii) slice crystal horizontally and vertically
  - (iii) polish and etch slices
  - (iv) evaluate for crystal properties
- If evaluation shows negative results, then add more dopant and repeat process

Six mixes each of germanium and gallium doped silver were prepared by melting together the metal and dopant, allowing time for mixing and then cooling rapidly by withdrawing the melt from the furnace. The weighed amounts of dopant added to these melts were sufficient to produce average doping levels as shown in Table 6.

TABLE 6

AVERAGE DOPING LEVELS OF SILVER CHARGES

Ag & Ge	Ppm Ge	Ag & Ga	Ppm Ga
Mix 1	755	Mix 1	3149
Mix 2	735	Mix 2	1032
Mix 3	376	Mix 3	1621
Mix 4	296	Mix 4	3430
Mix 5	895	Mix 5	2433
Mix 6	277	Mix 6	2742

The concentration of germanium in six doped silver crystals was measured by atomic absorption and the results are given in the following table. The sampling was accomplished by cutting a ring around the sample at three different locations.

TABLE 7

CONCENTRATION (PPM) OF GERMANIUM IN SILVER CRYSTALS

Crystal No.	Top	Center	Bottom
1	823	677	524
2	727	658	713
3	492	522	403
4	276	307	595
5	584	610	872
6	584	463	691

The distribution coefficient K for the germanium dopant in the silver was calculated from the equation.

$$C/Co = K(1-g)^{K-1}$$

Here K is the effective distribution coefficient, C the point concentration, Co the average concentration, and g the fraction of the length paralleling the axis of solidification. The sampling at the bottom of the crystal is at g = 0.1, the center at g = 0.5, and the top at g = 0.9.

The average effective distribution coefficient calculated for the germanium doped silver crystal was K = 0.89.

The crystals were cut horizontally and vertically to expose the growth patterns so that crystal imperfections such as striations, lamella, and homogeneity could be determined. It was at this point that problems arose. The silver crystals, as well as the gold-copper alloy crystals, are extremely soft, thus very vulnerable to deep surface damage. After a crystal was cut and polished an undamaged surface could not be exposed with a chemical etchant. The remaining time was spent in trying to find a polishing etch and an etch that would develop etch pits without extreme surface damage. Consequently the optimum doping level was not found.

Before the data obtained can lead to a firm conclusion, this phase needs further investigation, including a study of etching and polishing both silver and the gold-copper alloy.

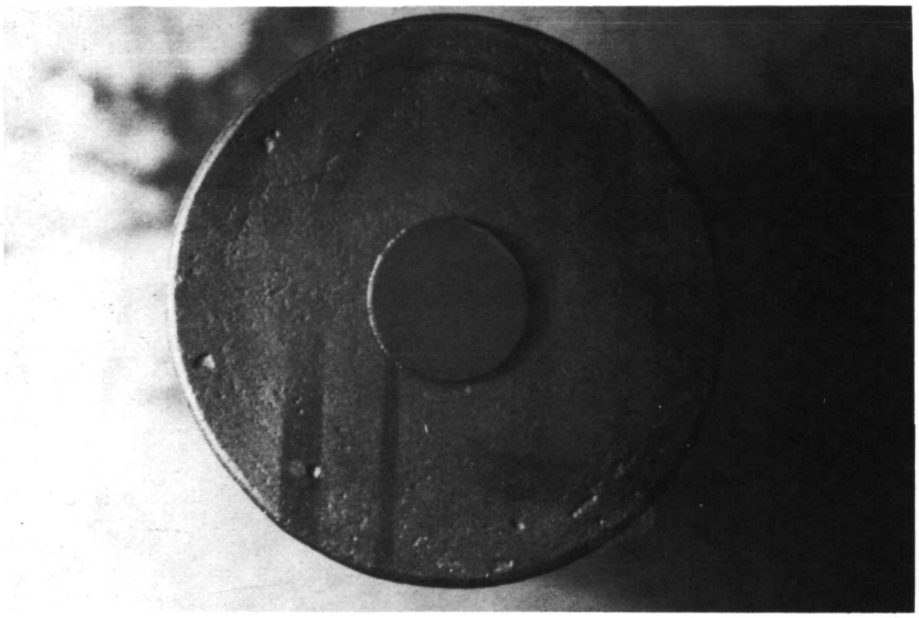
SINGLE CRYSTAL DATA FOR COMPARISON TO SPACE-GROWN CRYSTALS

The objective of this task was to obtain ground based data on the crystal parameters that are most likely to be affected by zero gravity. These parameters are the effective distribution coefficient, impurity segregation, alloy homogeneity, ordering of the alloys and crystal perfection. These data are needed for comparison purposes to identify crystal growth differences between space and terrestrially grown crystals. This task was not accomplished due to the difficulties in producing an undamaged surface and finding a suitable etchant, since the required information was to have been obtained from etch pit observation.

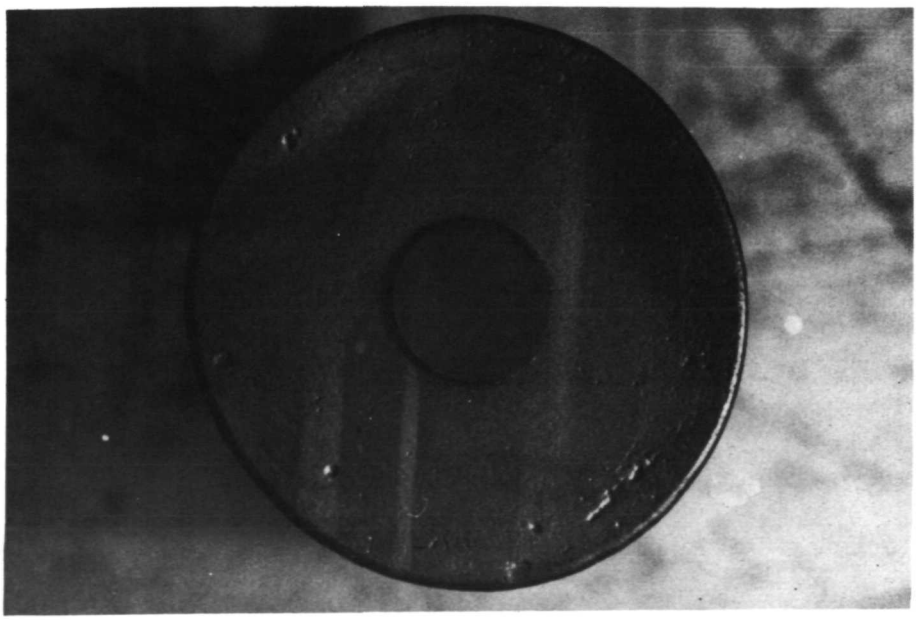
It is recommended that this task be accomplished after the problems of etching and polishing are solved. Only at that time can data be obtained that will produce good comparitive information.

Photographs were taken of the complete crystals and some of these are included on the next few pages. The scant information gained for these photographs are noted next to each.

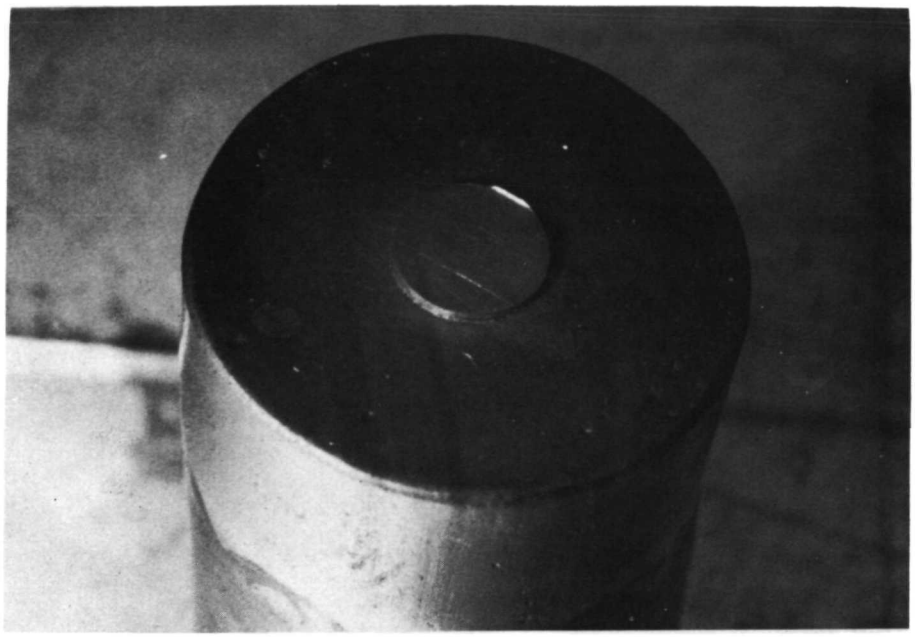
The crystal of gold-copper (Photographs 1 through 4) was etched by sputtering the surface off onto a target, which was tried as a last possibility. Its surface is greatly damaged on a microscopic scale. From the pictures parallel crystalline structure can be seen on the bottom and extending up the sides. These are twin lamellae which apparently extend the length of the crystal and show on part of the surface.



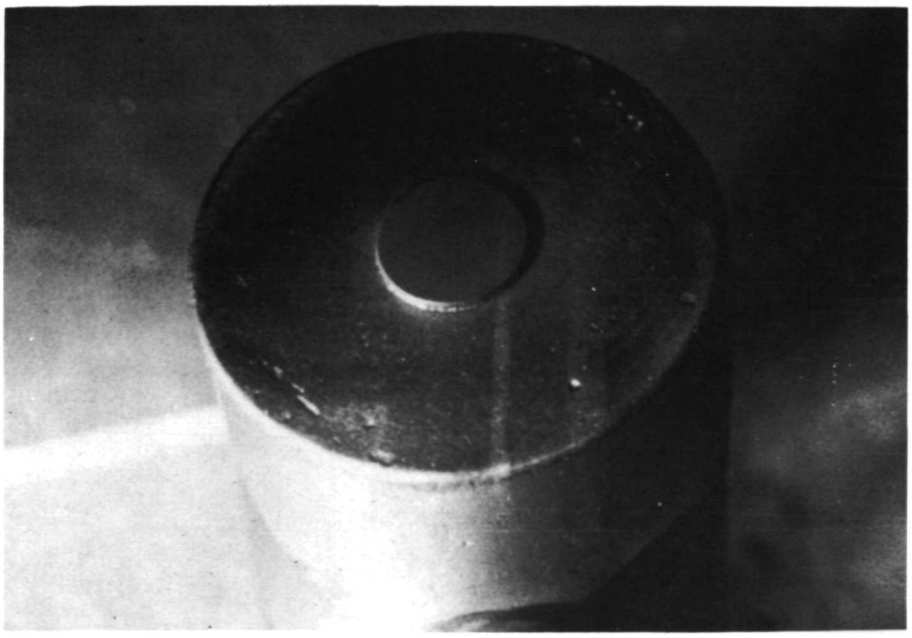
Photograph 1. Bottom of Gold-Copper Crystal showing the twin lamellae



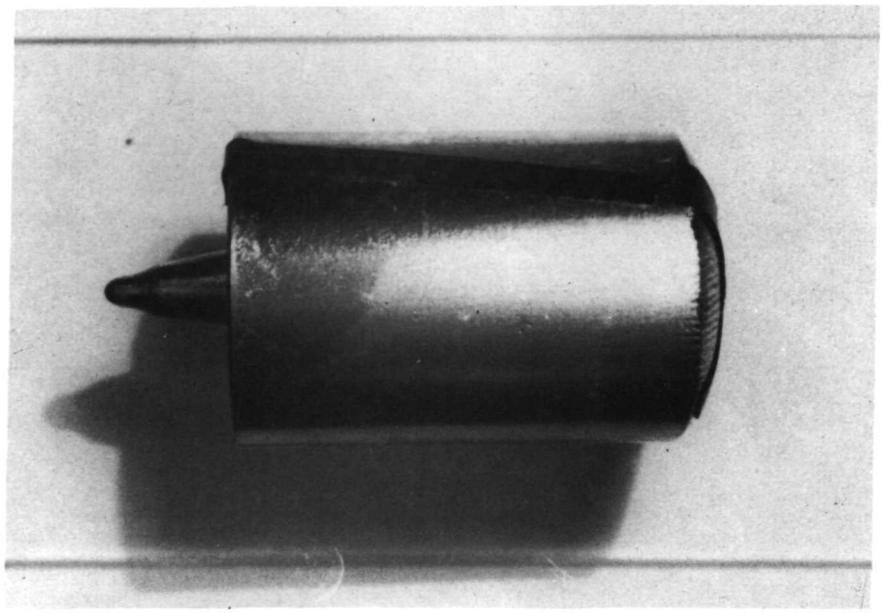
Photograph 2. Same crystal as #1 above, but with different lighting to contrast crystal orientation



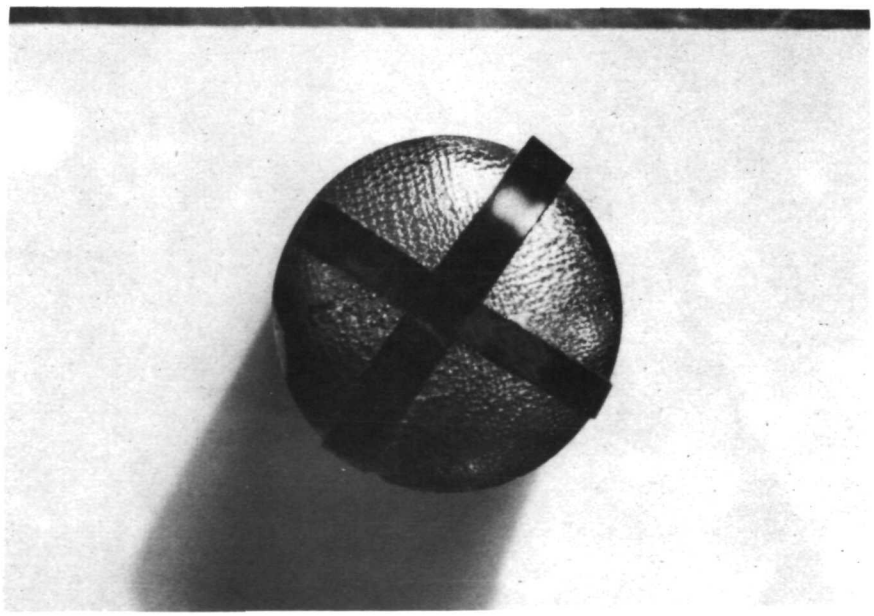
Photograph 3. Twin lamellae shown extending up the sides of the gold-copper crystal



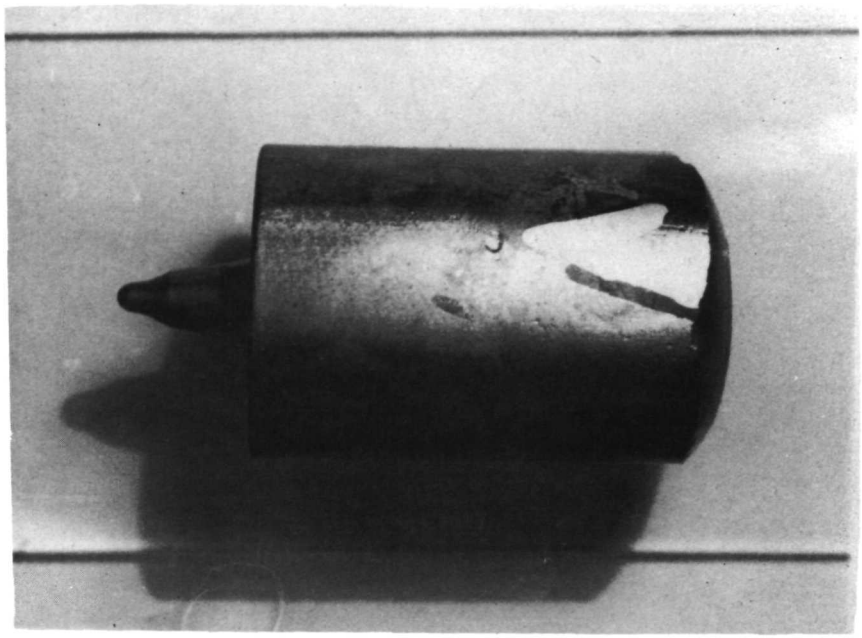
Photograph 4. Same crystal as #3, but with different lighting to contrast crystal orientation



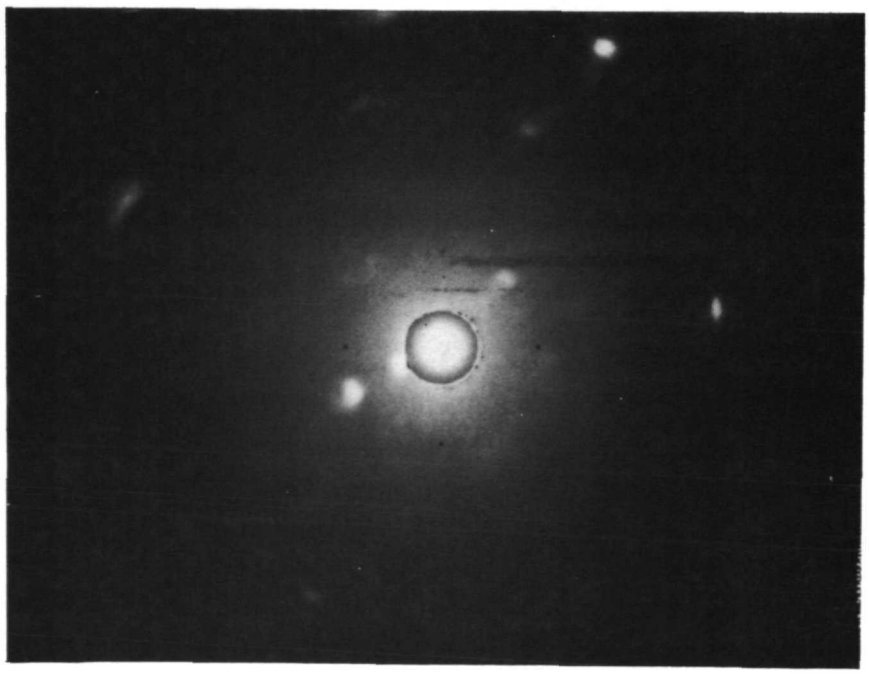
Photograph 5. Gold-copper single crystal with tape to indicate its orientation as determined by x-ray



Photograph 6. Gold-copper single crystal with tape to indicate its orientation as determined by x-ray

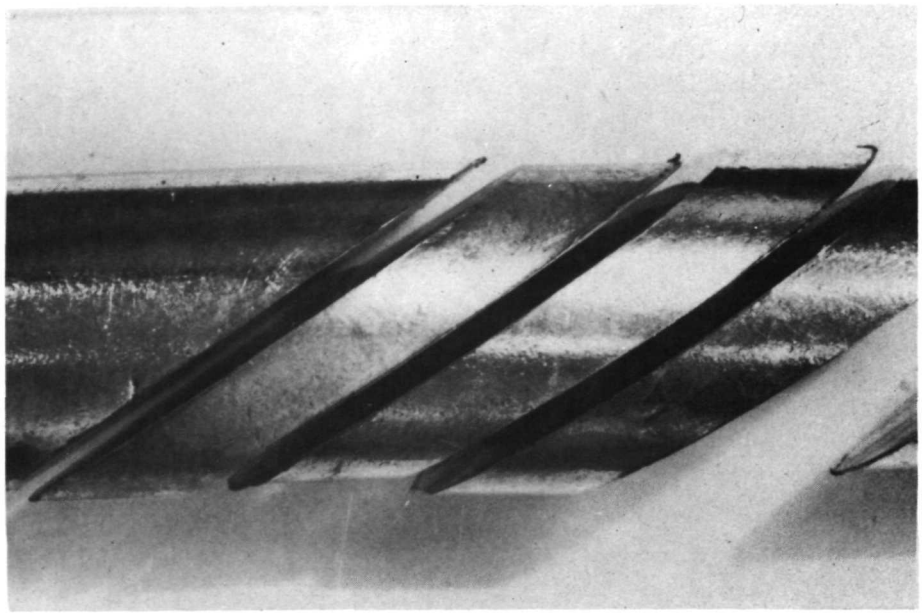


Photograph 7. Polycrystalline Gold-Copper

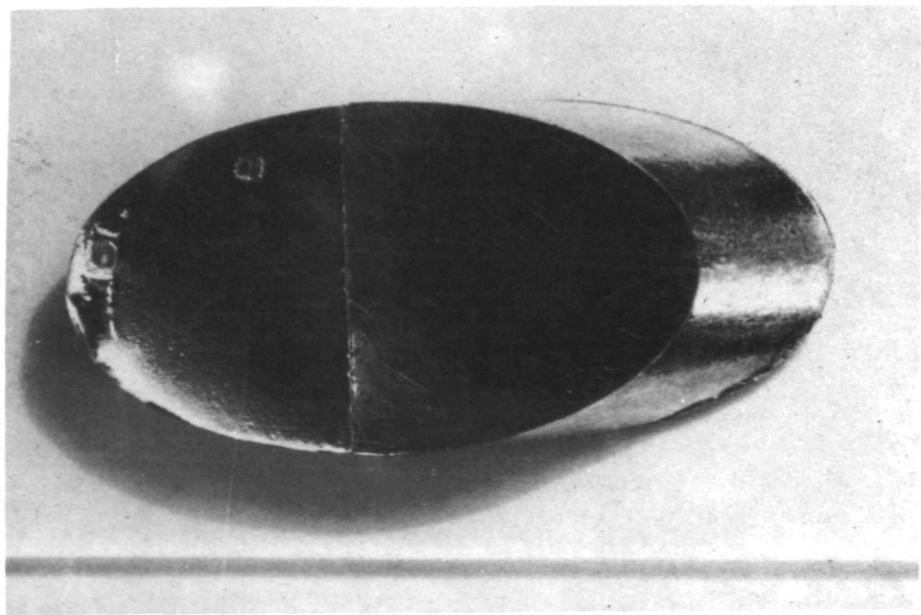


Photograph 8. X-ray pattern of a polycrystalline gold-copper ingot which is not the one above

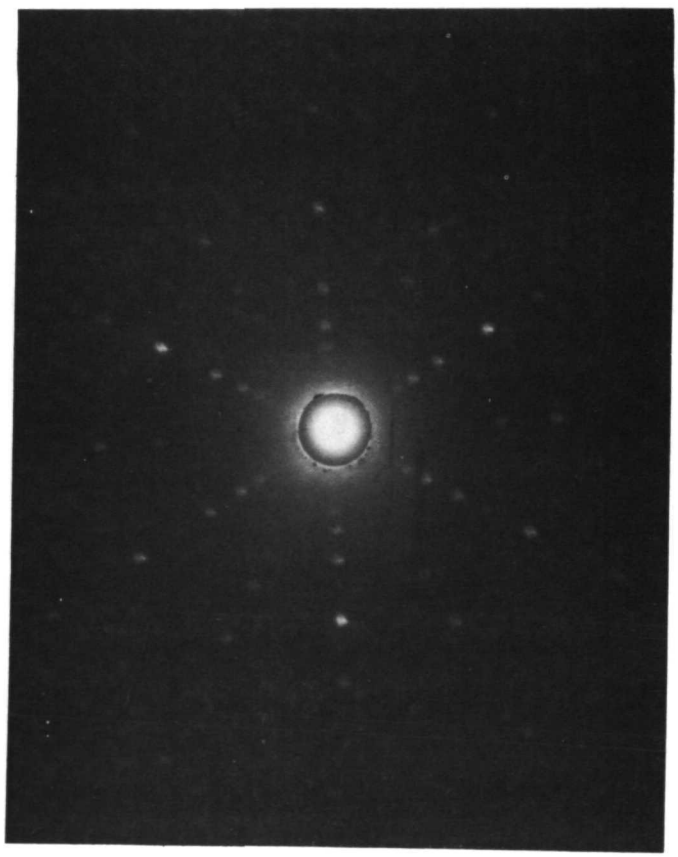
Photograph 9. X-ray Laue' pattern of the 100 directions on a single crystal of gold-copper



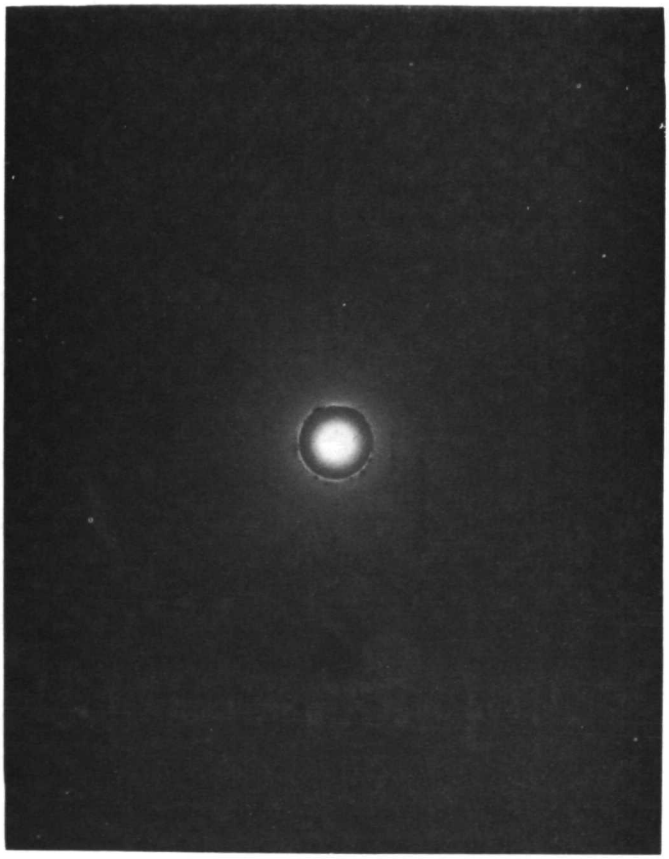
Photograph 10. Silver crystal cut to expose the 111 surfaces



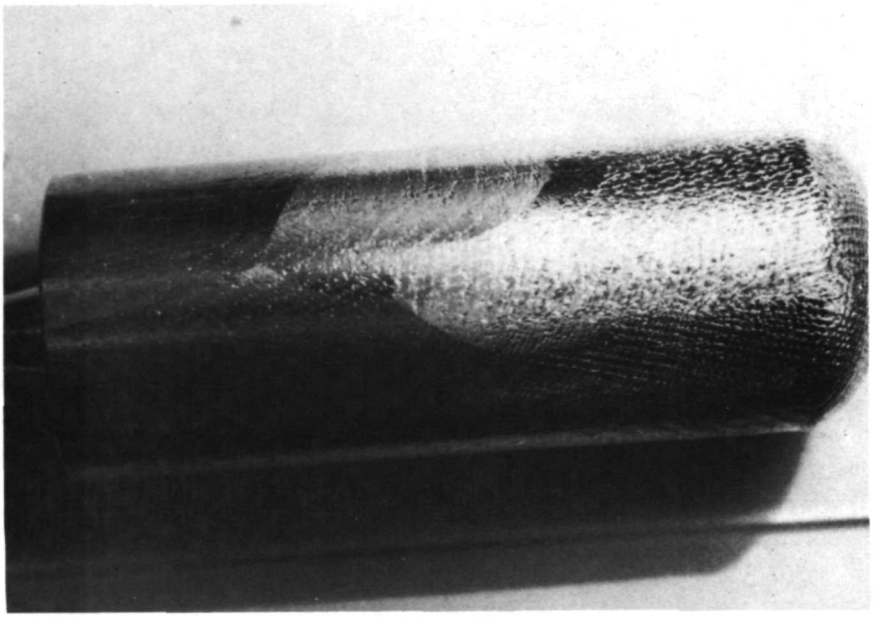
Photograph 11. Slice from the above crystal polished and etched. The surface damage was too much to obtain any useable information from a Laue' x-ray pattern nor from visible microscope viewing



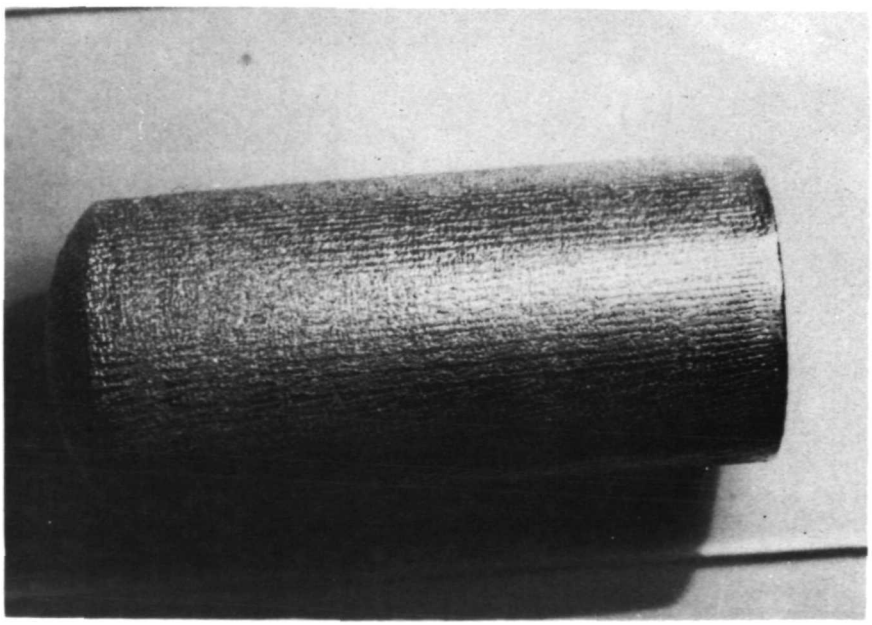
Photograph 12. X-ray Laue' pattern showing the 111 direction of the previous silver single crystal



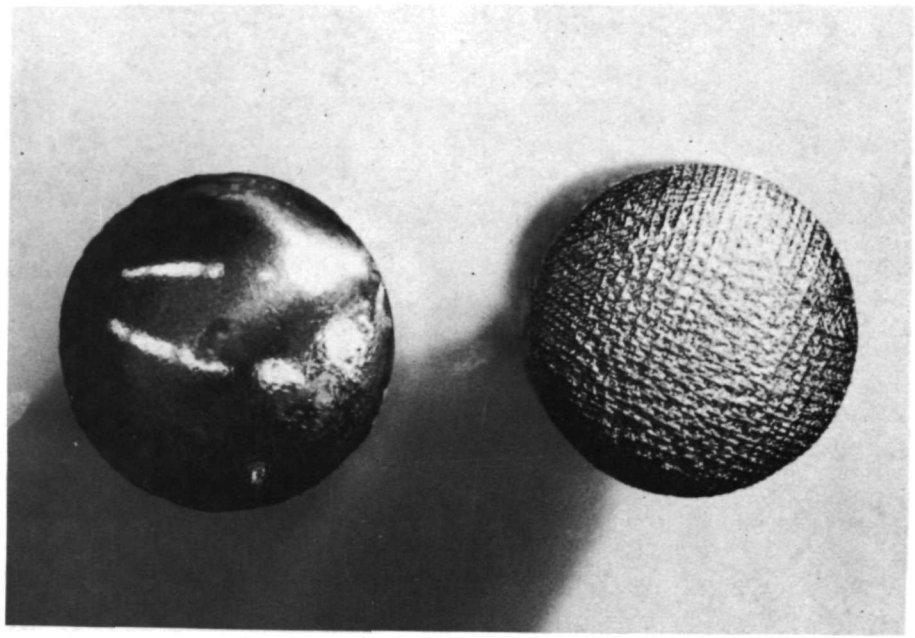
Photograph 13. X-ray Laue' of slice showing the surface is so damaged that the Laue' pattern is ruined



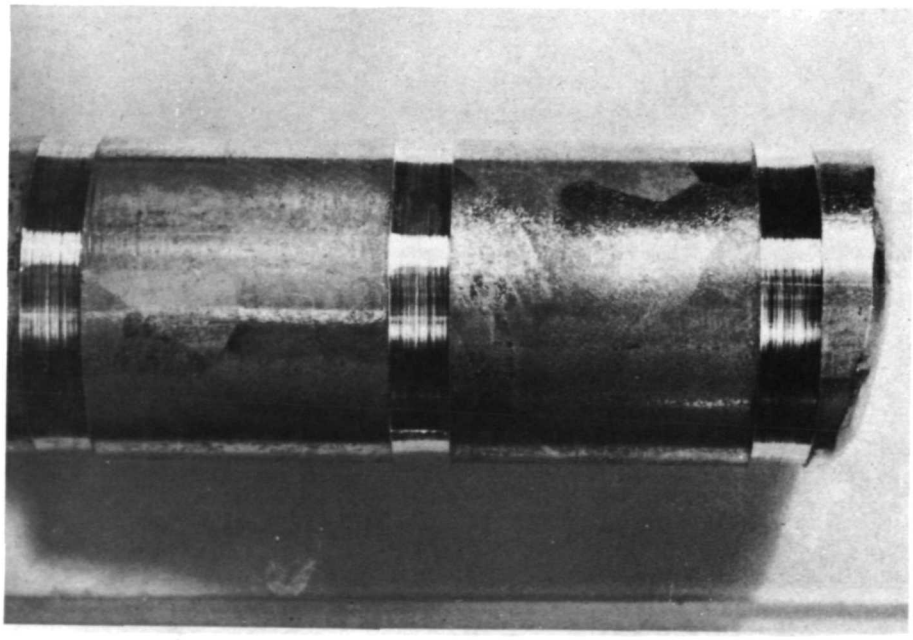
Photograph 14. Polycrystalline silver ingot



Photograph 15. Single crystal silver that was grown too fast



Photograph 16. Top of two silver crystals. The one with the smooth surface was grown with the correct parameters. The crystal with the patterned surface was probably annealed too long at too high a temperature



Photograph 17. Polycrystalline doped silver ingot showing the method of sampling for impurity concentration level

AMPOULE DESIGN

An ampoule was designed for crystal growth in space so that it would fit into a spacecraft experimental facility such as the "Multipurpose Electric Furnace System for Space Experiments" for Skylab. A Bridgman-Stockbarger type of seeding arrangement was used in the design of the crucible. Two slightly different seed chambers are shown in Figure 5, first,to grow silver single crystals,a neck is used at the upper end of the seed chamber. The second design is a conical shape, in which the gold-copper crystal is seeded. These two designs were required since the gold-copper crystal was difficult to remove from the crucible when using a seed chamber with a neck.

Graphite was used as the crucible material which was selected because the silver and gold-copper melts did not wet its surface. The crucible was machined from ECV grade graphite from Union Carbide. An evacuated quartz envelope was used to seal the crucible for use in space and to prevent contamination while growing the crystal. The quartz envelope was designed with features for pulling the ampoule through the furnace.

This combination of graphite crucible and quartz envelope has a usable maximum temperature (1300°C) far above that which will be used in this experiment. The ampoule can be exposed to almost any usable temperature gradient (2000°C/cm or greater)

without failure due to thermal shock, but it is limited in mechanical strength and mechanical shock which will break if hit sharply with a hard object. For small charges the melt sometimes does not flow into the seeding chamber, therefore, a larger seeding neck must be used. If the charge is fifty (50 grams) or less the diameter of the neck should be 1.59 mm (1/16") and a diameter of 1.19 mm (3/64") for larger charges. These measurements allowed full seeding chambers and did not inhibit the crystal growth process.

Figure 5 is a drawing of the ampoule showing the measurements and other specifications. The graphite is machined from rod stock and the quartz is welded from tubular stock of standard size.

The ampoule was loaded and the quartz sealed in according to the following procedure.

- The charge was cleaned with the appropriate etchant (HNO_3 for Ag and 10% KCN + 10%$(NH_4)_2S_2O_8$ for AuCu), washed with H_2O, isopropol alcohol, and H_2O.
- Dry the charge in a low temperature oven with a slight vacuum.
- Weigh the charge
- Place the charge in the graphite crucible and place it inside the quartz envelope. (a quartz rod is inserted through the evacuation tube to aid in lowering the crucible into the envelope slowly.)

- Weld on the bottom of the quartz envelope using a dry ice wrap around the rest of the envelope to prevent overheating of the charge.

- Pull a hard vacuum using a diffusion pump and seal off the envelope as close as possible to the graphite crucible (placing a shape in the seal for attaching a platinum wire.)

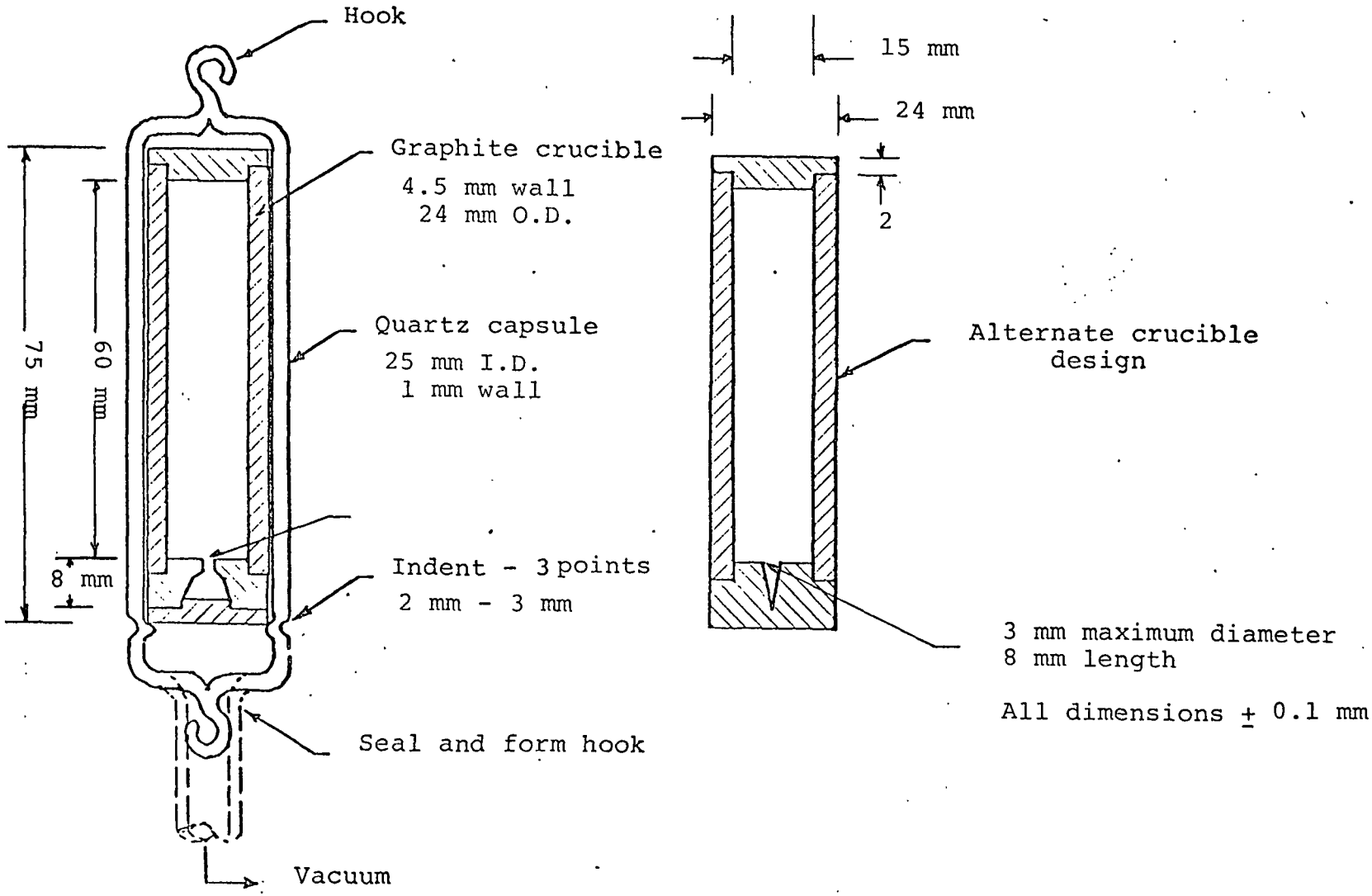


FIGURE 5. QUARTZ CAPSULE AND CRUCIBLES

CHARACTERIZATION PLAN FOR SPACE GROWN CRYSTALS

This section is an evaluation plan for determining the characteristics of the crystals grown in space and returned to earth for analysis. This plan recommends the sequence and techniques by which the crystals can be characterized with the maximum information yielded. The properties of the crystal which are to be measured are: effective distribution coefficient, impurity segregation, alloy homogeneity, ordering of the alloys, and crystal perfection. A short discussion of the cause of these defects has been presented in a previous section. The techniques for measuring these properties, and thereby characterizing the crystal, are given in the following paragraph. The detailed procedures are not given in this paper which assumes they are standard and known.

Orientation of Crystals

Before any analyses are performed, the space grown crystal, whether it is pure metal, doped, or alloy must be oriented (if polycrystalline the major crystals must be oriented.) The crystal is prepared by cutting off the seed of the crystal and by cleaning the exterior surface. The crystal is then mounted in a crystalographic x-ray machine and oriented through the use of back scattering patterns. The crystal is marked to indicate the crystal orientation.

Analysis of Alloy Crystals

Alloy Homogeneity Determination:

The crystal is cut vertically, along the axis of growth and then cut horizontally, so that crystal is exposed laterally and longitudinally. These surfaces are polished and etched by a polishing etch first and then etched to bring out the crystal boundaries, orientation, and compositional differences. This may be done on the quarters or thin slices of the surfaces. The surfaces are visually inspected for inhomogeneous areas at magnifications of 1X, 40X, and 100X using light and dark field viewing, and polarizers for complete investigations. Photographs are taken for a permanent record. X-ray topography should be used as a supplemental method and may be either the transmission Borrmann method or a reflection technique such as the Berg-Barrett method or the Lang method.

Alloy Ordering Determination:

With the crystal oriented and cut vertically and horizontally, a cut is made perpendicular to a crystal axis, if the crystal was determined to be single. This surface is polished, etched, and visually inspected at 100X, and 200X for crazing with a good metalographic microscope. If the AuCu crystal has not been annealed slowly through the solid-solid phase transition then it tends to change crystal structure to the lower temperature phase. As it spontaneously orders itself because of internal stress, the single crystallinity will be destroyed even for large crystallites in a polycrystalline ingot. The crazing, which may appear as a random etch pattern or a checked (triangular) pattern, is an indication of the ordering. The x-ray

backscattering patterns should also give an indication and x-ray topography should be used as a supplemental method of determination.

Analysis of Doped Metal Crystals

Impurity Segregation Determination:

With the crystal oriented previously, the crystal is cut vertically and horizontally, polished and the damaged surface etched away. Two methods should be used to determine the impurity segregation, a qualitative method, and a quantitative method. The qualitative technique would be to make an autoradiograph which can be accomplished after crystal preparation and if a dopant was used that can be activated. Slices are taken from both of the longitudinal and transverse surfaces. These slices are exposed to an activation source such as a neutron beam. The photographs, obtained by placing the slice on covered film, show where the impurity is concentrated and the relative amount. The qualitative measurement must be accomplished after all other analyses have been made. The sections which were not exposed to the radioactivation environment are to be sampled at a location near the seed, near the center, and near the top of the crystal. These samples, preferably taken in a band around the crystal, are subjected to chemical analysis such as atomic absorption, emission or mass spectroscopy.

Varying these quantitative measurements, an effective distribution coefficient is calculated with the proper equation.

Analysis of Crystals

All crystals have been oriented by x-ray methods, then cut vertically and horizontally, polished and the damaged surface etched away. The orientation in one or two of the quarters are checked by x-ray and these quarters cut perpendicular to a selected crystal plane. This cut is polished and etched to expose the undamaged surface of the selected crystal plane.

Crystal Perfection Determination:

The surface perpendicular to the crystal plane is examined by x-ray backscattering to determine if the crystalline structure has imperfections. This surface should be subjected to x-ray topography, reflection techniques and on slices transmission techniques. The surface is then etched to produce etch pits and a visual inspection is made, at magnifications of 100X and 200X, of the geometry of the etch pits. Any change of etch pit geometry over the surface of the slice would denote a change of crystalline structure.

Crystal Imperfections:

Striations, lamella, lineage, and slippage are the crystal imperfections that are of primary interest. These use the same method of determination and rely on different patterns and indications for identification. The methods, listed in order of preference, that are used to determine these imperfections are: x-ray topography, etch pit (100X and 200X) and autoradiography in the case of doped crystals. An electron scanning microscope should also be

used for an additional method. These techniques are used on all of the prepared surfaces in order to gain as much information as possible.

Sequence of Analyses

This section has been written in the preferred order of analyses with the one exception, that being the quantitative measurement of the impurity segregation. This sampling of the crystal destroys part of the crystal and thus, it should be left to the very last measurement. The neutron activation destroys the crystal on a microscopic scale and should be considered as the next to the last measurement. Therefore, all autoradiographic analyses should be made at the same time, so that only one activation would need be done.

SUMMARY

The objective of this program was to study the growth of single crystals of relatively high melting point metals such as silver, copper, gold, and their alloys. The purpose was to develop background information necessary to support a space flight experiment and to generate ground based data for comparison. The ground based data, when compared to the data from space grown crystals, are intended to identify any effects which zero-gravity might have on the basic process of single crystal growth of these metals.

The ultimate purposes of the complete investigation are to: determine specific metals and alloys to be investigated; grow single metal crystals in a terrestrial laboratory; determine crystal characteristics, properties, and growth parameters that will be effected by zero gravity; evaluate terrestrially grown crystals; grow single metal crystals in a space laboratory such as Skylab; evaluate the space grown crystals; compare for zero-gravity effects on crystal characteristics, properties, and parameters; and make a recommendation as to production of these crystals as a routine space manufacturing process.

This particular program encompassed an analytical study of the growth parameters and requirements, and the possible effects of zero-gravity on the growth of the metal single crystals. Single crystals of pure and doped silver, and 50% (at.) gold-copper alloy were grown by the Bridgman-Stockbarger technique. These crystals were evaluated for defects in the single crystal, material parameters,

and crystal growth parameters. A characterization plan for the evaluation of crystals grown in space was written and an ampoule for growing single crystals in space was designed.

The findings of this investigation of growing single crystals of relatively high melting point metals are summarized below in outline form.

The experimental requirements are:

- Determination of crystal properties and parameters
- Comparison between space grown and earth grown crystals
- Specifications of a space manufacturing facility

The typical furnace requirements are:

- Resistance type 1000°C furnace
- Two zones with baffle and 60 - 160°C temperature difference
- Temperature gradient 30 - 300°C/cm between zones
- Baffle hole diameter 2.5 cm
- Furnace length at least 25 cm
- Pull mechanism, 1 - 10 cm/hr vibration free
- Programmed temperature controller 20 - 2000°C/hr
- Ampoule - graphite crucible sealed in quartz under a vacuum - 2 cm x 8 - 10 cm

The material parameters for silver, germanium, and copper-gold alloy are:

	Ge	Ag	CuAu
. Melting temperature °C	936	960	880
. Latent heat of fusion, Kcal/mole	8.1	2.7	-

	Ge	Ag	CuAu
. Preferred crystal orientation	111	-	-
. Solid-solid phase transition	none	none	410°C
. Tendency to supercool growth	yes	yes	yes
. Dopant distribution coefficient	known	known	N/A
. Shrink upon freezing	no	yes	yes

The zero-gravity effects on crystal property are:

Primary effects

- No density separation in the melt
- No convection currents in the melt
- Free floating melt

Secondary effects

- Diffusion mixing of constituents and impurities which causes the distribution coefficient to be one
- Homogeneous crystal from immiscible components
- Fewer striations
- More perfect lamella structure
- More tendency to supercool
- Difficult seeding because of free floating melt

When a true vibrationless platform is achieved, it may help produce a more perfect single crystal.

From the list of metals and alloys in last paper, silver, germanium, and (50%at.) gold-copper alloy were selected to be studied. These were selected by the following criteria:

Silver

- The only metal by all definitions

Germanium

- Best known properties and imperfections

Gold-Copper

- Wider constituent range (70% at.)
- Metal compounds exist
- Solidus and liquidus lines meet
- Order-disorder alloy due to solid-solid phase transition

The materials used to measure each of the parameters are:

- Distributive coefficient - Ag or Ge (doped)
- Impurity segregation - Ag or Ge (doped)
- Homogeneity - (50% at.) Au-Cu
- Crystal perfection - Ag or Ge (pure or doped), or AuCu
- Liquid-solid transition - Ag or Ge (pure or doped), or AuCu
- Striations - Ag or Ge (doped), or AuCu
- Lineage and slippage - Ag or Ge (pure or doped), or AuCu
- Lamella-AuCu

Three furnace designs were tested with one meeting the requirements. The furnace that was used has the following capabilities:

- Usable temperature range 100°C - 1200°C
- Zone temperature difference 0°C - 200°C
- Temperature gradient at baffle 0°C/cm - 300°C/cm
- Pull mechanism - continuously variable from 0.7 cm/hr to 55 cm/hr
- Cooling rate - manually controlled
- Baffle hole diameter 2.54 cm (1 inch)
- Furnace length 25.4 cm (10 inches)

The following crystals were produced:

10 gold-copper (single crystals)

12 silver (single crystals)

2 silver (polycrystalline)

4 gold-copper (polycrystalline)

and numerous polycrystalline scrap silver

The range of the growth parameters that were used to grow single crystals of silver are:

. Upper zone temperature	975°C - 1005°C
. Temperature difference of zones	52°C - 73°C
. Temperature gradient	81°C - 115°C/cm
. Hold time at melt temperature	1 hour

- Pull rate 2.3 cm/hr - 6.7 cm/hr
- Pull length 8 cm
- Cooling rate 432°C/hr - 515°C/hr
- Temperature at power cut-off 552°C - 606°C
- Vacuum in ampoule 0.03 Torr - 0.09 Torr

The range of the growth parameters that were used to grow single crystal gold-copper alloy are:

- Upper zone temperature 895°C - 915°C
- Temperature difference of zone 50°C - 78°C
- Temperature gradient 78°C/cm - 122°C/cm
- Hold time at melt temperature 1 hour
- Pull rate 3.3 cm/hr - 11.7 cm/hr
- Pull length 8 cm
- Cooling rate 160°C/hr - 310°C/hr
- Temperature at power cut-off 295°C - 360°C
- Vacuum in ampoule 0.03 Torr - 0.09 Torr

The procedures for single crystal growth of the silver and gold-copper alloy were established. The data table from a silver crystal growth is included.

Single crystals of silver doped with germanium were grown. Silver ingots doped with gallium were to be grown into single

crystal when the problem of polishing and etching stopped any further progress. After a crystal was cut and polished,an undamaged surface could not be exposed with a chemical etchant. The remaining experimental time was spent trying to find a polishing etch and an etch that would develop pits without extreme surface damage. Consequently the optimum doping level was not found.

An ampoule design is presented with a procedure for filling and sealing it.

A characterization plan and sequence for space grown crystals evaluation is presented for:

- Orientation of the crystal by x-ray backscattering
- Inhomogeneity determination by x-ray topography and visual
- Determination of ordering by x-ray topography and visual
- Impurity segregation by autoradiography and visual (and effective distribution coefficient calculated)
- Crystal perfection by x-ray and etch pit patterns
- Crystal imperfections by x-ray topography, visual autoradiography, and electron scanning microscope

CONCLUSIONS AND RECOMMENDATIONS

From the analytical study and the experimental investigation, a number of conclusions can be drawn. Their findings lead to conclusions, that in the case of the analytical study, are almost probabilistic. The conclusions are firm facts in the case of the experimental investigation.

The advantages of growing single crystals of silver, germanium, and gold-copper alloy in a space environment are no convection currents exists, and no separation and settling out of immiscible mixture of metal liquids. These will produce different effects in the space grown crystal. The effective distribution coefficient would be approximately one, and inhomogeneity, lineage, slippage, and striation may be eliminated or reduced greatly; unless the increase in supercooling off-sets the advantages from not having convection currents. The lamella produced by some alloys would tend to be more pronounced and more perfect.

This analytical study of the parameters, requirements and zero-gravity effects on single crystal growth of metals in space concludes that there are definite advantages to space growth of metal crystals. There will be many crystal characteristics that will be changed for the better and the zero-gravity environment should enhance crystal perfection.

In the experimental investigation the procedures, parameters, and experimental limits were established. Single crystals of gold-copper, silver, and doped silver were grown. It was determined

that a doping level exists, past which a single crystal of silver cannot be grown, but an optimum doping level was not determined. Problems occurred when a good polishing and chemical etching method was not found. A chemical polishing etchant that would expose the undamaged surface would allow this project to progress.

It is recommended that a method of polishing and etching the silver and gold-copper surfaces be established before trying to obtain further data. The preliminary data for comparison should be taken after the polishing and etching procedures are almost routine. It is further recommended that after this preliminary comparison data are taken, that the comparison data be taken by the methods that are recommended in the Characterization Plan. It is also recommended that crystals of these materials be grown in various orientations with respect to the gravatational vector. These crystals should be compared to the crystals grown vertically in order that gravity dependent crystal growth characteristics can be identified with more certainty. It is further recommended that this experiment be performed in space because of the good possibilities of a better single crystal.

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